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Louis P. Hammett, Ph.D., *Consulting Editor*

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A Course in

INORGANIC PREPARATIONS

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A Course in
Inorganic Preparations

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PREFACE

It is the conviction of the authors that a course in the preparation of a series of pure compounds is an invaluable introduction to other courses in chemistry. It may constitute a part of advanced work of the college course or may be undertaken upon entrance to graduate work. Fortunately, a very effective course may be planned within the limits of the laboratory equipment of any good college, and in selecting the present exercises all unusual or costly apparatus has been avoided.

The fault of many books designed to meet this need has been that they were too narrowly recipe books which gave the student little impulse to associate a given preparation with any principle in chemistry, either as an operation or as representative of a class of compounds. Most of the exercises in this book are to be found in some one of the large or small books giving directions for inorganic preparations. Whatever merits this volume may have will lie not so much in the novelty of the examples selected as in the organization of the material around definite methods of procedure and as illustrative of classes of compounds.

It is not expected that any one student will complete all these exercises, but rather that assignments will be made in such a way as to insure a variety of work in progress in the laboratory. It is also expected that there will be frequent quizzes on the pedagogical material in the text that will serve as a review and an extension of the more fundamental courses in inorganic chemistry. The additional exercises following many of the exercises afford opportunity for some originality in modifying the details of a given process and for emphasizing the fact that each case presents its own problems.

The handbooks cited are almost exclusively the two best known English works: "Textbook of Inorganic Chemistry," edited by J. N. Friend; and the monumental "Comprehensive Treatise on Inorganic and Theoretical Chemistry" of J. W. Mellor. Occasionally other handbooks are cited, especially in connection with topics not as yet covered by the two already mentioned. Instructors in charge of graduate courses may prefer to direct their students to some of the well-known German works of the same type.

Insofar as possible, we have sought to supply references to the journals of the American Chemical Society, as being available in all college libraries. The references to European journals are usually to the original description of the compound or to a much improved method of preparation. Occasionally, references are to some specific monograph. The student should be made to feel that a most important part of his work is to read widely about the preparation on which he is engaged and on topics suggested by it and that the mere mechanical following of directions largely defeats the purpose of the course.

The character of the notes to be required of the student is best left to the instructor. Certainly the student should not be asked to write out the exact procedure that he has followed, for this is given in detail in the exercises. It is equally obvious that he should write all the equations for the reactions involved in the exercises that he undertakes.

It may be added that the material presented here has been in process of growth with many classes and over a period of a good many years. It is believed that, if carefully followed, the directions will give satisfactory results.

THE AUTHORS.

THE OHIO STATE UNIVERSITY,
June, 1935.

CONTENTS

PAGE
Preface v
Foreword to the Student xv
Abbreviations Used in References xvii
Object of the Course 1

PART I

PREPARATIONS ILLUSTRATING GENERAL METHODS OF MANIPULATION

I. Crystallization 3
  1. Simple Recrystallization 3
    Exercise 1. The Recrystallization of Potassium Sulfate . 6
    Exercise 2. The Recrystallization of Potassium Nitrate. 8
  2. Recrystallization in the Presence of Isomorphous Impurities 8
    Exercise 3. The Purification of Copper Sulfate. 9
  3. Recrystallization after Chemical Removal of Impurities . 12
    Exercise 4. The Purification of Common Salt. . . . 12

II. Obtaining Hydrated Crystals in Good Condition. . . . 13
  1. Efflorescence 14
    Exercise 5. Hydrated Sodium Sulfate. 15
  2. Supersaturation. 16
    Exercise 6. Hydrated Lead Acetate. 16
  3. Deliquescence. 18
    Exercise 7. Calcium Nitrate 19

III. Protection from the Action of the Air 20
  1. Protection from Oxidation 20
    Exercise 8. Ferrous Sulfate 20
    Exercise 9. Ferrous Chloride. 22
    Exercise 10. Cuprous Chloride. 24
  2. Protection from Carbon Dioxide. 27
    Exercise 11. Crystallized Barium Hydroxide. 27
  3. Protection from Moisture—Hydrolysis 29
    Exercise 12. Ferric Nitrate. 30
    Exercise 13. Antimony Sulfate 32

PAGE
IV. DOUBLE DECOMPOSITION 33
Exercise 14. Calcium Carbonate—Precipitation. . . . 35
Exercise 15. Cupric Chloride—Recovery of a Soluble Salt 36
Exercise 16. Crystallized Barium Thiosulfate—Diffusion 39

V. DISTILLATION 41
Exercise 17. The Distillation of Mercury 41
Exercise 18. Nitrogen Dioxide 44
Exercise 19. Sulfur Dioxide 48

VI. THE PROCESS OF SUBLIMATION 49
Exercise 20. The Purification of Arsenous Oxide 49

VII. FURNACE METHODS 50
Exercise 21. Chromic Oxide 52

VIII. ELECTROLYTIC PROCESSES 52
Exercise 22. Barium Ferrate 53
Exercise 23. Lead Chromate 55

PART II

PREPARATIONS ILLUSTRATING TYPES OF COMPOUNDS

I. BINARY COMPOUNDS 57
1. The Union of Two Elementary Substances 58
Exercise 24. Mercuric Sulfide (Vermilion) 58
Exercise 25. Magnesium Nitride 60
Exercise 26. Sulfur Monochloride; Phosphorus Trichloride; Stannic Chloride 62
2. Double Decomposition 64
Exercise 27. Stannous Sulfide 66
Exercise 28. Crystalline Stannic Sulfide 66
3. The Preparation of a Chloride by the Action of Sulfur or Carbon Chloride upon an Oxide 67
Exercise 29. Anhydrous Chromic Chloride 68
4. The Preparation of a Hydride 69
Exercise 30. Hydrogen Bromide, Hydrobromic Acid . . 70
5. Reduction of Ternary Compounds 73
Exercise 31. Strontium Sulfide 73

II. INTERMETALLIC COMPOUNDS; SALTS OF HOMOATOMIC ANIONS 74
Exercise 32. Sodium Polyplumbide; Sodium Polystannide 76
Exercise 33. Magnetic Alloys of Manganese and Antimony 77

PAGE
III. THE PREPARATION OF SALTS 77
1. Normal Salts 77
2. Acid Salts 78
Exercise 34. Potassium Tetroxalate. 78
3. Basic Salts 79
Exercise 35. Basic Lead Chromate 79
Exercise 36. Basic Lead Nitrate 79
Exercise 37. Antimony Oxychloride. 80
Exercise 38. Beryllium Basic Acetate 81

IV. PREPARATION OF HYDROGEN SALTS (ACIDS) 82
Exercise 39. Hydrogen Arsenate 83
Exercise 40. Hydrogen Phosphate 83
Exercise 41. Hydrogen Iodate 84

V. PREPARATION AND REACTIONS OF OXYGEN SALTS. 86
1. Salts of Ordinary Oxygen Acids 86
a. Oxidizing Salts 86
Exercise 42. Potassium Perchlorate. 87
b. Reducing Salts 87
1. Reduction of a Higher Salt. 88
Exercise 43. Sodium Nitrite 88
2. Neutralization 89
3. Action of a Nonmetal on a Soluble Base. 89
Exercise 44. Barium Hypophosphite 90
4. Special Methods 91
Exercise 45. Zinc Hyposulfite 91
2. Salts of Metallo-acids 92
Exercise 46. Potassium Permanganate. 93
Exercise 47. Potassium Hydrogen Pyroantimonate . . . 94
Exercise 48. Salts of Ferric Acid 95

VI. PER-ACIDS AND THEIR SALTS. 96
1. Preparation by Anodic Oxidation 97
Exercise 49. Potassium Persulfate 97
2. Preparation by Action of Hydrogen Peroxide on Acids or Their Salts 98
Exercise 50. Sodium Perborate. 99
Exercise 51. Potassium Perchromate 99
Exercise 52. Potassium Pervanadate 100

VII. DISSOCIABLE COMPOUNDS 100
Exercise 53. Phosphonium Iodide. 101

PAGE

VIII. CRYSTALLIZATION FROM SOLUTIONS CONTAINING TWO OR MORE SALTS . . . 103
  1. Double Salts . . . 104
    Exercise 54. Ferrous Ammonium Sulfate (Mohr's Salt) . 109
    Exercise 55. Potassium Chrome Alum . . . 110
    Exercise 56. Ammonium Iron Alum . . . 111
  2. Complex Salts . . . 112
    Exercise 57. Sodium Cobaltinitrite . . . 113
    Exercise 58. Sodium Nitroprusside . . . 114
  3. Fluoacids and Chloroacids . . . 115
    Exercise 59. Fluosilicic Acid . . . 115
    Exercise 60. Potassium Fluotitanate . . . 117
    Exercise 61. Chlorostannic Acid . . . 118

IX. THE POLYACIDS AND THEIR SALTS . . . 119
    Exercise 62. Phosphomolybdic Acid . . . 120
    Exercise 63. Potassium Phosphomolybdate . . . 120
    Exercise 64. Ammonium Arsenitungstate . . . 121
    Exercise 65. Ammonium Phospho-vanadiotungstate . . . 121
    Exercise 66. Ammonium Phospho-vanadicotungstate . . 122

X. THE ACTION OF WATER AND OF AMMONIA UPON METALLIC SALTS . . . 122
  1. Ammonates—Analogues of Hydrates . . . 126
    Exercise 67. Tetrammino-cupri Sulfate . . . 126
    Exercise 68. Carbonato-tetrammino-cobalti Nitrate . . . 128
    Exercise 69. Chloro-pentammino-cobalti Chloride . . . 128
    Exercise 70. Trinitrito-triammino-cobalt . . . 129
    Exercise 71. Hexammino-chromic Nitrate; Chloro-pentammino-chromic Chloride . . . 130
    Exercise 72. Fusible White Precipitate . . . 131
  2. Ammono Basic Salts . . . 132
    Exercise 73. Infusible White Precipitate . . . 132
  3. Mixed Aquoammono Base . . . 132
    Exercise 74. Millon's Base; Salts of Millon's Base . . . 132

XI. THIO SALTS . . . 133
  1. Salts Analogous to Well-known Oxygen Salts . . . 133
    Exercise 75. Potassium Trithiocarbonate . . . 134
    Exercise 76. Barium Trithiocarbonate . . . 134
    Exercise 77. Ammonium Cuprous Trithiocarbonate . . . 135
    Exercise 78. Sodium Thioantimonate (Schlippe's Salt) . 135
  2. Double Sulfides . . . 136
    Exercise 79. Potassium Ferrisulfide . . . 136
    Exercise 80. Ammonium Tetrathio-cuprate . . . 137

PAGE
3. Salts of Thionic Acids 137
  Exercise 81. Sodium Thiosulfate 138
  Exercise 82. Barium Dithionate 138

XII. CHLORIDES OF THE OXYGEN ACIDS 140
  Exercise 83. Sulfuryl Chloride 140
  Exercise 84. Chromyl Chloride. 143

XIII. ALUMINOTHERMIC REDUCTION 143
  Exercise 85. Metallic Manganese. 145
  Exercise 86. Chromium 146
  Exercise 87. Silicon. 146

XIV. ELECTROCHEMICAL REPLACEMENT 147
  Exercise 88. Preparation of Potassium Iodate from Potassium Chlorate 147

XV. TRANSITION POINTS IN SALTS 148
  Exercise 89. Cuprous Iodomercurate 149
  Exercise 90. Silver Iodomercurate 150
  Exercise 91. Potassium Cupric Chloride. 151
  Exercise 92. Calcium Cupric Acetate 152

XVI. METALLO-ORGANIC COMPOUNDS (GRIGNARD'S SYNTHESIS) . . 152
  Exercise 93. Lead Tetraphenyl. 152

PART III

THE COLLOIDAL STATE OF MATTER

I. MODES OF PREPARING COLLOIDS. 157
  1. Crystallization Methods 157
    1. By Change in the Solvent--Gum Mastic—Silver Iodide. 157
    2. By Processes of Reduction. 158
    Exercise 94. Purple of Cassius 158
    Exercise 95. Red Gold Sol. 158
    Exercise 96. Colloidal Silver. 159
    3. By Processes of Double Decomposition 160
    Exercise 97. Colloidal Antimony Sulfide. 160
    Exercise 98. Colloidal Ferric Hydroxide. 161
  2. Solution Methods 162
    Exercise 99. Colloidal Cadmium Sulfide. 162
  3. Method of Electrical Dispersion (Bredig's Method) . . . 162
    Exercise 100. Colloidal Platinum. 162

PAGE
II. DIALYSIS TESTS FOR COLLOIDS 164
Exercise 101. Preparation of the Dialyser 164

III. GELS 166
1. Production of Gels by Double Decomposition 167
Exercise 102. Gel of Silicic Acid 167
Exercise 103. Gel of Cupric Hydroxide 167
2. Production of Gels by Hydrolysis 168
Exercise 104. The Gel of Stannic Hydroxide 168
Exercise 105. The Gel of Chromic Hydroxide 168
3. Production of Gels by Reduction of the Salts of Metallo-acids 169
Exercise 106. The Gel of Chromic Hydroxide 169
Exercise 107. The Sol and Gel of Manganese Dioxide . 169
Exercise 108. The Gel of Ferrous Hydroxide 170

IV. RHYTHMIC BANDS—LIESEGANG RINGS 171
Exercise 109. Banded Mercuric Iodide 172
Exercise 110. Banded Copper Chromate 172

V. CRYSTAL GROWTH IN GELS 173
Exercise 111. Gold Crystals 173
Exercise 112. Copper Crystals 174
Exercise 113. Lead Iodide Crystals 174

VI. EMULSIONS 175
Exercise 114. Emulsions of Oil in Water 175
Exercise 115. Emulsions of Water in Oil 176
Exercise 116. Emulsions of Paint and Linseed Oil 177

INDEX 179

FOREWORD TO THE STUDENT

1. Each exercise is chosen to illustrate some definite process, principle, or type of compound. The object of the exercise must be steadily kept in mind.

2. Each student should read ahead at least a day's work in his assignment and should be prepared to ask all necessary questions when the instructor makes his rounds.

3. Do not undertake too many preparations at the same time; and push each one to a conclusion as rapidly as possible.

4. Confine your work to your own desk top, which must be kept neat and clean.

5. Hold yourself responsible for cleaning up after a break on the hot plate, under a hood, or on the floor by your desk.

6. Do not leave a vessel on the hot plate or water bath, under a hood, or in an air oven longer than necessary, and label all vessels with your name.

7. Exercise the greatest care with burners. No burner or furnace is to be left lighted unless some one is present in charge of it.

8. Corrosive chemicals, particularly nitric acid, must be emptied into waste jars and not into the sinks. No solid materials should ever be emptied into the sinks.

9. All chemicals must be kept in bottles, appropriately labeled. None should be left in desks wrapped in paper.

10. Residues of inflammable chemicals, particularly phosphorus (either yellow or red), must be disposed of with especial care. If possible, they should be burned or thrown into jars containing water.

11. The reagents in bottles on the work desks are for tests only and are not in general of concentration adapted for preparations.

12. Excess materials, not wanted as specimens, should be placed in large labeled bottles for common use in later experiments.

ABBREVIATIONS USED IN REFERENCES

HANDBOOKS AND DICTIONARIES

Ephraim: A Textbook of Inorganic Chemistry, translated by Thorne, 2d ed., Gurney & Jackson, London, 1933.
Friend: Textbook of Inorganic Chemistry, J. B. Lippincott Company, Philadelphia.
Mellor: A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Longmans, Green & Company, New York, 1928–1932.
Thorpe: Dictionary of Applied Chemistry, Longmans, Green & Company, New York, 1934.
Watts: Dictionary of Chemistry, revised by H. F. Muir and M. M. Pattison Morley, Longmans Green & Company, New York.

JOURNALS

Am. Chem. J.	*American Chemical Journal.*
Am. J. Sci.	*American Journal of Science.*
Ann.	*Annalen der Chemie* (Liebig).
Ann. chim. phys.	*Annales de chimie et de physique* (since 1914, *Annales de chimie*).
Ann. Physik	*Annalen der Physik* (which appeared at various times as Gilbert's, Poggendorff's, Wiedemann's, and Drude's *Annalen*).
Arch. Pharm.	*Archiv der Pharmazie.*
Atti accad. Lincei	*Atti della reale accademia nazionale dei Lincei.*
Ber.	*Berichte der deutschen chemischen Gesellschaft.*
Bull. soc. chim.	*Bulletin de la société chimique de France.*
C. A.	*Chemical Abstracts.*
Chem. Met. Eng.	*Chemical and Metallurgical Engineering.*
Chem. News	*Chemical News.*
Chem. Reviews	*Chemical Reviews.*
Chem. Zentr.	*Chemisches Zentralblatt.*
Chem. Ztg.	*Chemiker Zeitung.*

Compt. rend.	*Comptes rendus hebdomadaires des séances de l'académie des sciences.*
Gazz. chim. ital.	*Gazzetta chimica italiana.*
Helv. chim. Acta.	*Helvetica Chimica Acta.*
J. Am. Chem. Soc.	*Journal of the American Chemical Society.*
J. Chem. Educ.	*Journal of Chemical Education.*
J. Chem. Soc.	*Journal of the Chemical Society* (London).
J. Franklin Inst.	*Journal of the Franklin Institute.*
J. Ind. Eng. Chem.	*Journal of Industrial and Engineering Chemistry* (since 1923, *Industrial and Engineering Chemistry*).
J. Phys. Chem.	*Journal of Physical Chemistry.*
J. prakt. Chem.	*Journal für praktische Chemie.*
J. Soc. Chem. Ind.	*Journal of the Society of Chemical Industry.*
Monatsh.	*Monatshefte für Chemie und verwandte Teile anderer Wissenschaften* (Vienna).
Kolloid-Zeit.	*Kolloid-Zeitschrift.*
Proc. Chem. Soc.	*Proceedings of the Chemical Society* (London).
Proc. 8th Int. Cong. Appl. Chem.	*Proceedings of the Eighth International Congress for Applied Chemistry.*
Proc. Roy. Soc.	*Proceedings of the Royal Society* (London).
Quart. J. Sci.	*Quarterly Journal of Science.*
Trans. Am. Electrochem. Soc.	*Transactions of the American Electrochemical Society.*
Trans. Faraday Soc.	*Transactions of the Faraday Society.*
Z. anal. Chem.	*Zeitschrift für analytische Chemie.*
Z. angew. Chem.	*Zeitschrift für angewandte Chemie.*
Z. anorg. Chem.	*Zeitschrift für anorganische Chemie* (since 1915, *Zeitschrift für anorganische und allgemeine Chemie*).
Z. Elektrochem.	*Zeitschrift für Elektrochemie.*
Z. phys. Chem.	*Zeitschrift für physikalische Chemie.*

A COURSE IN INORGANIC PREPARATIONS

Object of the Course.—In the laboratory exercises which constitute the working portion of this text, directions are given for the preparation of a number of chemical substances in more or less pure condition.

The object in undertaking such a series of preparations is twofold: (1) the acquisition of a certain degree of skill in dealing with the difficulties that are encountered in the process of making pure compounds; and (2) the extension and classification of information regarding types of compounds, acquaintance with the methods available in their preparation, and acquaintance with their chief reactions. This should include familiarity with the colloidal state of matter which any material may assume.

Accordingly, in the earlier exercises, 23 in number, attention is centered on *methods of manipulation* for overcoming the usual varieties of difficulties and in gaining experience in the use of preparative processes. Later exercises are arranged with reference to a number of *types of compounds* and the reactions available for their preparation. A final group of exercises is provided to illustrate the chief *characteristics of colloidal systems.*

PART I

PREPARATIONS ILLUSTRATING GENERAL METHODS OF MANIPULATION

Note: When possible, the references following each exercise should be consulted by the student. Information about most of the compounds may also be found in the dictionaries of Watts or Thorpe.

I. CRYSTALLIZATION

The simplest problem that presents itself in the preparation of pure chemical materials is the purification of an impure specimen. In the case of many liquids, this is accomplished by fractional distillation; in the case of some solids, it may be effected by the process of sublimation; but for the most part, it is done by crystallization. For the present, attention will be directed to this last process.

1. Simple Recrystallization.—In the simplest procedure of recrystallization, the salt is dissolved in some appropriate hot solvent, and the solution is then allowed to cool to room temperature. All the salt in excess of the weight soluble at the lower temperature crystallizes and may be filtered from the mother liquor. Insoluble impurities remain undissolved and may be removed by filtering the hot solution before crystallization begins; soluble impurities remain in the solution from which the crystals separate. It is evident that this simplest process applies to the purification of salts that have a decided difference of solubility at different temperatures; to cases in which the soluble impurity is not too abundant, or too sparingly soluble; and to cases in which the compound to be purified does not form crystals isomorphous with those of any impurity present, leading to the formation of solid solutions.

References on Crystallography and Crystallization: Friend, I, 47; Mellor, I, 589, 623, 633; Moore, *J. Am. Chem. Soc.*, **41,** 1060 (1919).

Before proceeding with the recrystallization of a given salt, the student should look up its solubility (expressed in tables or plotted curves (Fig. 1), since the mode of procedure will depend to some extent upon the rate at which solubility increases with the temperature. If the increase is fast, it is clear that a solution saturated at its boiling point will deposit crystals very rapidly as it cools and that as a result the crystals will be very small

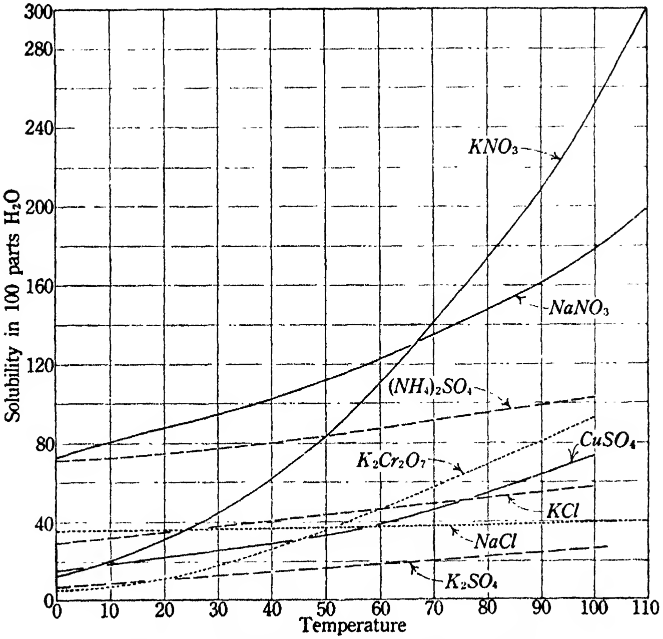


FIG. 1.—Solubilities of some common salts.

and imperfect. In such a case, it is better to saturate the solution at a lower temperature in order to secure slower cooling. If the solubility of the salt increases rather slowly with the temperature, the solution should be saturated at a higher temperature near the boiling point.

In general, it is not desirable to obtain large crystals, since no two crops will look alike. The best preparation will consist of small crystals not larger than a grain of wheat, as uniform in size as possible, not too much matted together, but not necessarily of perfect form.

References on Solubility: Comey and Hahn, A Dictionary of Chemical Solubilities (Inorganic); Seidell, Solubilities of Inorganic and Organic Compounds; Landolt-Börnstein, Physikalisch-Chemische Tabellen; International Critical Tables.

Notes of Filtration.—From the outset, the student should cultivate proper habits in regard to filtration.

For the removal of a relatively small quantity of solids which filter easily, a filter paper should be chosen that when folded will not entirely cover the inside surface of the funnel, and it should be so folded as to fit exactly the angle of the funnel. It should be wet with water before using.

If a considerable quantity of a solid is to be removed, it is of advantage to use a folded or fluted filter paper. Directions for proper folding and use should be sought from the instructor.

If suction is to be employed, a platinum cone must be used to support the tip of the filter paper; or a Witte plate or a Büchner funnel may be used with a paper that just fits the flat, perforated surface.

Crystals are usually washed on a bare Witte plate or Büchner funnel, using a paper on the plate only when necessary.

If a precipitate tends to stop the pores of filter paper (very fine crystals or colloidal jellies), a filter may be made by placing a spherical marble in the throat of the funnel. This arrangement may be made still more efficient by bedding the marble on an asbestos string or pouring a suspension of shredded asbestos over the marble (if the precipitate is to be discarded). A more stable arrangement is obtained by using a bulb blown on the end of a short piece of glass tubing. The tubing should be small enough to slip easily into the stem of the funnel, and after the bulb has been blown, the tube should be sealed off about an inch beyond the bulb. This stem, slipped into the funnel tube, steadies the bulb.

In all cases, if the precipitate at first runs through the filter, the filtrate should be returned to the funnel until good filtration is secured.

EXERCISE I. THE RECRYSTALLIZATION OF POTASSIUM SULFATE, K_2SO_4

The tables of solubility show that at 20° about 11 g. of potassium sulfate dissolves in 100 g. of water, while at 100° about 24 g. dissolves. Crystals will therefore form rather slowly from a cooling saturated solution.

Powder 25 to 30 g. of commercial potassium sulfate in a mortar. In a 500-cc. evaporating dish heat 100 cc. of water to boiling and in small portions at a time add the powdered salt, stirring well after each addition. If a little of the salt refuses to dissolve, add water in small quantities until all the salt has been brought into solution at the boiling point. Add about 5 cc. of water, heat to boiling, and filter through a folded filter into a beaker of suitable size, to remove insoluble impurities. If some of the salt crystallizes in the beaker during the filtration, heat the filtrate until it again dissolves. Set the beaker aside to cool, taking care to avoid placing it on any good-conducting surface such as a table top of stone or metal, for this will chill the bottom of the beaker and produce a cake of small matted crystals.

When the solution is quite cold, bring the crystals on to a bare Witte plate or Büchner funnel, using a portion of the filtrate to wash them out of the beaker. Pump off the mother liquor with a water pump, washing the crystals with one or two portions of cold water. Combine the filtrate from the crystals with the wash water and evaporate the solution for another crop of crystals. Boil the solution until a rather persistent ring of solid salt tends to form at the line where the surface of the solution touches the evaporating dish; then set the dish aside to cool. The second crop of crystals may be added to the first, and the two dried together.

Since the crystals are anhydrous, no special precautions are necessary in drying them. They should be spread out on a sheet of filter paper on a clean glass plate and covered with paper to protect them from dust. Only when they are completely dry should they be placed in bottles. They should rattle as they are shaken on paper. The impulse of the student is almost always to bottle them too soon.

To decide as to the purity of such a preparation, it is usually sufficient to test the sample for the particular impurities which the mode of manufacture of the salt suggests as most probable. In the present case, the absence of chloride and magnesium ions may be taken as proof of purity.

References on Potassium Sulfate: Friend, II, 173; Mellor, II, 657.

References on Impurities in Chemicals: Krauch, The Testing of Chemical Reagents for Purity, p. 256 (1902); Murray, Standards and Tests for Reagents and C. P. Chemicals, p. 408 (1927); Schade, *J. Am.*

Chem. Soc., **28,** 1422 (1906); Buc, *J. Ind. Eng. Chem.*, **11,** 1140 (1919).

Topic: Manufacture of potassium sulfate.

References: Dictionaries and texts on industrial chemistry.

Additional Exercises: Potassium dichromate, $K_2Cr_2O_7$; potassium chlorate, $KClO_3$.

EXERCISE 2. THE RECRYSTALLIZATION OF POTASSIUM NITRATE, KNO_3

The tables of solubility show that at 20° about 32 g. of potassium nitrate dissolves in 100 g. of water while at 100° about 246 g. dissolves (Fig. 1). From a hot, saturated solution the salt deposits too rapidly to give good crystals, for the rate of radiation depends upon the difference between the temperature of the solution and that of the room. Modify the procedure of Exercise 1 as follows:

Heat 100 cc. of water in a 500-cc. evaporating dish to about 60°. Add powdered commercial potassium nitrate in small portions at a time with frequent stirring until no more will dissolve. This should require about 110 g. If all of the added salt fails to dissolve, add a little hot water to effect complete solution. Heat the solution somewhat short of boiling, and filter through a folded filter, catching the filtrate in a beaker of suitable size. Set the beaker aside to cool, and when it is cold proceed as in Exercise 1. In evaporating the mother liquor for a second crop, a too concentrated solution will be obtained if the evaporation is carried to the point of forming a ring of solid material on the sides of the dish. Instead, the solution should be evaporated to about half its volume and then set aside to crystallize.

References: Friend, II, 179; Mellor, II, 802; Krauch, p. 248; Murray, p. 393.

Additional Exercises: Sodium nitrate, $NaNO_3$; lead nitrate, $Pb(NO_3)_2$.

2. Recrystallization in the Presence of Isomorphous Impurities.—In general, when two salts that are capable of forming isomorphous crystals are present in a solution, the crystals that are deposited on crystallization are solid solutions containing both salts. These are, in general, not present in the crystals in the same ratio as in the solution, and by a great many recrystallizations it is possible to bring about a separation, but the process is very slow and laborious. When possible, it is much better to convert the salt impurity into a form that is no longer isomorphous with the salt desired. It may then be removed by simple recrystallization or by a chemical reaction that will remove it as a precipitate, leaving the desired salt in solution. The purification of commercial copper sulfate affords a good illustration of these principles, for as a rule it is contaminated with isomorphous ferrous sulfate.

References on Isomorphism: Friend, I, 70; Mellor, 1, 651; Langmuir, *J. Am. Chem. Soc.*, **41**, 1543 (1919).

References on Fractional Crystallization: Soch, *J. Phys. Chem.*, **2**, 43 (1898); Evans, Metals and Metallic Compounds, vol. II, p. 231 (1923); Ephraim, A Textbook of Inorganic Chemistry, p. 790 (trans. by Thorne), 2d ed. (1934).

EXERCISE 3. THE PURIFICATION OF COPPER SULFATE, $CuSO_4 \cdot 5H_2O$

As a *preliminary experiment* to prove that simple recrystallization will not remove ferrous sulfate from copper sulfate, proceed as follows:

Dissolve 500 g. of commercial copper sulfate (bluestone) in 1.5 l. of boiling water in an evaporating dish, add 3 g. of ferrous sulfate (unless this is known to be present as an impurity), and allow the solution to cool. Select about 1 g. of the crystals that form and test them for iron. To do this, dissolve the material in 10 cc. of water, add about 2 cc. of concentrated nitric acid, and boil for a few minutes. Cool the solution and add ammonium hydroxide until the copper hydroxide that separates at first has redissolved to form a deep purple-blue solution. Filter through a small filter of white paper, and wash with dilute ammonia or hot water until the blue color is washed out of the filter. A *reddish-brown* stain on the paper is ferric hydroxide. Throw away the deep-blue filtrate.

Drain the crystals of copper sulfate that have by this time accumulated in the original solution, if necessary evaporating the mother liquors from them to secure a second crop of crystals. Secure about half of the original material in this form and set aside the mother liquor for future use. Recrystallize the salt as in the original procedure, using a proportionate quantity of water. Again test a specimen of the crystals obtained for iron and convince yourself that it is still present. Those experiments show that the ferrous sulfate is not removed by several crystallizations.

Actual Purification.—To remove the iron, proceed as follows: Recombine all of the mother liquors and crystals (excepting the test portions to which ammonium hydroxide was added), bringing the volume back to about the original volume. Add 20 g. of lead peroxide, and boil the mixture for an hour, stirring it at frequent intervals and replacing the water as it evaporates. Take out 10 cc. of the solution filter from the suspended solids and test for iron as follows: To the filtrate add a few cubic centimeters of a thin paste made by shaking barium carbonate with water. Shake vigorously for a few minutes and again filter. Add ammonium hydroxide to the filtrate until the copper hydroxide dissolves to form a deep purple-blue solution. Filter through a small paper, washing with hot water until the blue color has been removed from the filter. A *reddish-brown* stain upon the paper shows the presence of iron. A yellow stain, due to the action of ammonia on lead sulfate, should not be mistaken as a test for iron. If iron is still present, add more lead peroxide and continue the boiling. From time to time test for iron, until it is no longer present, taking care not to add the test portions to the main solution.

When a test for iron is no longer obtained, dilute the solution to about its original volume and allow to cool. Add about 10 g. of barium carbonate in the form of a thin paste and stir the cold solution from time to time for about an hour. Filter and evaporate the solution until a ring of solid salt tends to form persistently on the dish at the line of contact with the liquid. Again filter if necessary, place the dish on an asbestos board or wooden desk top, and allow to cool. If no crystals have formed by the next morning, the solution must be evaporated somewhat further; if the crystals form a thick cake or are much matted together, water must be added, and the crystals again brought into solution for recrystallization. Sometimes a greenish precipitate forms on the bottom of the dish and even on the crystals. This is a basic salt of copper (how account for its formation?). In this case, the crystals must be dissolved in the mother liquor, the precipitate filtered from the hot solution, and the crystallization repeated; or a few cubic centimeters of sulfuric acid may be added to dissolve the precipitate.

Drain the crystals on a bare Witte plate or a Büchner funnel, wash them once or twice with small portions of cold water, and spread them to dry on clean filter paper supported on a glass plate. A second and third crop should be secured from the mother liquor.

References on $CuSO_2 \cdot 5H_2O$: Friend, II, 279; Mellor, III, 240; Krauch, p. **90**; Murray, p. 225; Foote, *Am. Chem. J.*, **26**, 418 (1901); Hopkins, *Am. Chem. J.*, **25**, 413 (1901); Schade, *J. Am. Chem. Soc.*, **28**, 1422 (1906).

References to Other Methods of Purifying Isomorphous Salts: Richards and Yngve, *J. Am. Chem. Soc.*, **40**, 91 (1918).

Additional Examples: $ZnSO_4 \cdot 7H_2O$ contaminated with $CuSO_4 \cdot 5H_2O$; $MgSO_4 \cdot 7H_2O$ contaminated with $ZnSO_4 \cdot 7H_2O$.

Topic: The barium carbonate method for separating trivalent and bivalent bases: Treadwell-Hall, Quantitative Analysis, vol. II, 151, 7th ed. (1928).

3. Recrystallization after Chemical Removal of Impurities.—In some cases, it is better to remove each known impurity by a definite chemical reaction and not depend upon crystallization as an assistance. This is especially true when the solubility of the preparation is not very different in hot and in cold water. In such cases, not only must all the original foreign substances be removed, but all excesses of added reagents must also be removed during the purification. In the last Exercise, this was accomplished by using insoluble reagents only; the purification of common salt is a good example of a different process. In addition to sodium chloride, commercial salt usually contains the calcium and magnesium ions and traces of iron and aluminum, together with the acid ions $SO_4^{=}$, Br^-, and I^-. The solubility of sodium chloride at 0° is 35.7 g. in 100 g. of water; and at 100°, 39 g. (Fig. 1).

EXERCISE 4. THE PURIFICATION OF COMMON SALT, NaCl

(Dissolve about 500 g. of common salt in 1,500 cc. of warm water. Heat well toward boiling and add 5 g. of lime which has been slaked and diluted to a thin paste with water (milk of lime). Add a dilute solution of barium chloride as long as the latter produces a precipitate. (This is rather difficult to determine, since the liquid is turbid. The best way is to pipette off a few cubic centimeters from near the edge of the dish and filter through a small filter, testing the filtrate with a few drops of barium chloride. On an average, it will require about 12 g. of crystallized barium chloride. When the precipitation is complete, add a solution of 15 g. of pure anhydrous sodium carbonate. Filter through a folded filter; bring the filtrate to the boiling point and carefully neutralize with pure, dilute hydrochloric acid. Boil the solution over a free flame until it has evaporated to a volume of about 500 cc. but do not allow it to go to dryness. If the evaporation is rapid, the salt separates in small, mealy crystals, a condition which is desirable in this case. If evaporation is slow, as on a hot plate, or if the solution is strongly acid, the crystals will be coarse and will inclose water mechanically. Bring the crystals on to a bare Witte plate or Büchner funnel, returning the filtrate to the funnel as long as crystals pass through the filter; then pump the crystals free from mother liquor with the water pump, pressing them down on the funnel with a spatula to prevent the formation of drainage channels through the wet mass. Spread the crystal meal in a clean evaporating dish and dry on the hot plate or in a drying oven. The preparation should be snow white and free from lumps and, if properly dried, should not decrepitate on heating. The product usually contains traces of potassium chloride. Write out all equations involved in the process of purification. Aside from sodium chloride, what remains in the mother liquor?

References on NaCl: Thorpe, Dictionary, V, 6, 195; Watts, Dictionary, IV, 476 (1924); Krauch, p. 283; Friend, II, 93; Mellor, II, 527.

II. OBTAINING HYDRATED CRYSTALS IN GOOD CONDITION

While it is usually not a difficult matter to secure crystals of some sort from a solution, it often requires some practice to get them to form in suitable condition for drying and preserving, and it is often still more difficult to accomplish the drying without bringing about some alteration in the crystals, such as efflorescence, deliquescence, oxidation, or hydrolysis.

1. Efflorescence.—Many salts containing water of crystallization tend to lose at least a portion of this water when exposed to the air in the process of drying. In such cases, it is a problem to remove all of the adhering mother liquor, leaving the crystals dry, and yet prevent loss of crystal water by efflorescence. All hydrated crystals may be regarded as maintaining a certain aqueous vapor pressure, which tends to result in loss of water. This tendency is opposed by the partial pressure of the water vapor normally present in the air. When the vapor pressure due to the salt is distinctly greater than the opposing aqueous pressure of the air, the salt will effloresce when exposed to the air. Efflorescence is therefore relative to the humidity of the air.

When the dissociation pressure of the hydrate is small, as with $CuSO_4 \cdot 5H_2O$, the drying of the salt presents no difficulty. Even when there is some disposition toward efflorescence, the crystals may be dried on paper in the usual way if they are stirred frequently and watched closely. At the first sign of efflorescence they should be bottled up. In many cases, however, some crystals will begin to effloresce while others are still wet with mother liquor. In such an event it is best to proceed as follows:

Take a portion of the crystals (or some of the material in crude form) and allow it to effloresce freely in a warm place. Put it in a roomy desiccator in place of the usual drying agent (calcium chloride). Place the wet crystals in a suitable container and support them over the effloresced material in the desiccator (Fig. 2). There are now three materials present, each with a different aqueous vapor pressure: the saturated mother liquor which moistens the crystals, the hydrated salt, and the effloresced salt. If there is free circulation of air in the desiccator, the latter salt will absorb moisture from the mother liquor but not from the hydrate. The hydrate will therefore become dry but not overdry.

Reference: Findlay: The Phase Rule, pp. 82, 6th ed. (1929); Friend, I, 176; Mellor, I, 502; Baker and Adlam, *J. Chem. Soc.*, **99, 507** (1911); *Proc. Chem. Soc.*, **27**, 17 (1911).

EXERCISE 5. HYDRATED SODIUM SULFATE, $Na_2SO_4 \cdot 10H_2O$

Dissolve about 250 g. of commercial sodium sulfate (Glauber's salt) in 800 cc. of water heated to 35°. (Look up the solubility curve of sodium sulfate to find the explanation for this direction.) If the salt is notably impure, the solution should be freed from iron by adding enough bromine water to oxidize the iron and then enough sodium hydroxide to make the solution distinctly alkaline. Filter the solution through a folded filter and set it aside in a quiet place to crystallize. The crystals are glassy in appearance and should not be too large or grown together. Drain them on a Witte plate and evaporate the mother liquor for a second crop. They may be obtained as needles; as lath-shaped crystals; or in a compact, many-sided form. The last named is the most desirable form, and conditions should be varied to avoid supersaturation (Exercise 6) until such crystals are obtained. Meanwhile, prepare some effloresced sodium sulfate by gently warming about 100 g. of the crude crystals until they fall into white powder. Place this powder in the bottom of an empty desiccator and

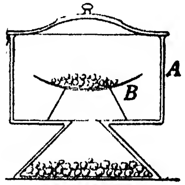


FIG. 2.

spread the wet crystals on a watch glass or a small evaporating dish in the upper part of the desiccator, being careful to provide for free circulation of the air in the desiccator (Fig. 2). Occasionally, stir the crystals about and allow them to dry until they will rattle on paper. Put them in a bottle and seal in the stopper with paraffin. Students always have the tendency to bottle preparations before they are sufficiently dry.

References: Mellor, II, 667; Friend, II, 117. If available, Faraday's original observations on the efflorescence of sodium sulfate should be consulted: *Quart. J. Science*, **19**, 152 (1825); Faraday's Diary, I, 169.

Additional Exercises: Manganese chloride, $MnCl_2 \cdot 4H_2O$; magnesium sulfate, $MgSO_4 \cdot 7H_2O$.

2. Supersaturation.—One of the most frequent difficulties in crystallization is due to *supersaturation.* This condition arises when the normal saturation concentration of a salt solution is exceeded without the appearance of any crystals, and as the solution cools further it becomes steadily more supersaturated. When crystallization finally starts, it proceeds with great rapidity, forming a mass of poorly defined crystals unsuited to drying. The tendency toward supersaturation is most marked in the case of very soluble substances which form viscous or syrupy solutions. Lead acetate, sodium thiosulfate, ferric nitrate, and sulfuric acid are good examples.

EXERCISE 6. HYDRATED LEAD ACETATE, $Pb(C_2H_3O_2)_2 \cdot 3H_2O$

Place 50 g. of litharge in an evaporating dish containing 75 cc. of water and add 22 g. of glacial acetic acid (or concentrated commercial acid) in small portions at a time, stirring after each addition. When all has been added, heat gently until action ceases. During the latter process, add a piece of clean lead to precipitate foreign metals that may be present in the litharge (what ones would be precipitated?). When the lead ceases to show a deposit of copper, dilute the mixture to about 150 cc. and filter hot through a fluted filter. If an insufficient quantity of acetic acid has been used, a basic salt will result (equation?), and this will not itself crystallize and will tend to prevent the good crystallization of the normal salt. The filtrate should be tested with litmus paper, and acetic acid should be added until it is strongly acid.

After filtration, evaporate until the ring of salt on the dish suggests that the solution is sufficiently concentrated to crystallize. On cooling the solution and allowing it to stand for a time, it is probable that it wi[illegible] to a solid cake. If this happens, add about [illegible] water, bring the salt into solution by heating, [illegible]nce more allow to cool. It will often happen that no salt will form on cooling. If this is the case, obtain a small crystal of the salt and add it to the solution. If the latter is supersaturated, this will start crystallization; if no crystals form within a short time, the solution must be evaporated, and the process repeated. The crystals ultimately obtained should be in the form of fine needles which, on drying on paper, will fall apart into individual crystals. Test a small quantity before proceeding further.

This process of "*seeding*" or "*inoculation*" should be resorted to before evaporating further in every case in which it is suspected that supersaturation has occurred. It is of advantage to proceed as follows: Evaporate until you feel certain that crystallization should occur on cooling. Obtain a little of the solid and powder it in a mortar. From time to time, dust a little of the powder into the solution as it cools. When saturation is reached, each of the dust particles becomes a center of crystallization, insuring the formation of many crystals, no one of which will be too large.

Having obtained a good crop of satisfactory crystals of lead acetate, bring them on to a bare Witte plate or Büchner funnel and pump them as dry as possible, pressing the crystals together with a porcelain spatula. Remove the cake from the funnel and spread the material on dry paper, moving the crystals about with the spatula at frequent intervals and watching for evidences of efflorescence. When the crystals are quite dry, so that they rattle on dry paper, put them in a bottle and seal in the stopper with paraffin. If the air happens to b[illegible]dry and warm that efflorescence cannot be preve[illegible]sort to the method described in the preceding exer[illegible]s.

References: Basic acetates of lead, Jackson, *J. Am. Chem. Soc.*, **36,** 2346 (1914); Supersaturation, Friend, I, 110; Mellor, I, 450.

Topics: Basic salts; electrochemical series of the metals; mechanical stimulus to crystallization in supersaturated solutions, Young, *J. Am. Chem. Soc.*, **33,** 148 (1911).

Additional Exercises: Calcium chloride, $CaCl_2 \cdot 6H_2O$; sodium thiosulfate, $Na_2S_2O_3 \cdot 5H_2O$.

3. Deliquescence.—It sometimes happens that a salt that has been crystallized and spread in the air to dry absorbs water instead of losing it and in time passes again into solution. This may occur with anhydrous salts as well as with hydrates but not so frequently. This conduct is readily understood if it is remembered that the process of drying is always dependent upon the equilibrium between the aqueous vapor pressure of the material undergoing drying and the partial pressure of the water vapor in the air. The vapor pressure of a salt solution is always lower than that of the pure solvent. When the solution is very concentrated, its vapor pressure may be so much lowered as to be less than the partial pressure of the water vapor in the air. In this case, the *solution* will absorb water from the air when exposed to it, instead of evaporating.

When, therefore, crystals of *very soluble* salts are drained and exposed to air, the mother liquor adhering to them tends to become diluted by absorption of atmosphere moisture. Some of the solid will then dissolve to saturate the dilute solution, and this process may finally carry all of the solid into solution. Deliquescence is therefore not to be attributed to any chemical affinity for moisture on the part of the salt *but to its great solubility*. Any very soluble salt is likely to be deliquescent, and a moderately soluble one will not be so.

EXERCISE 7. CALCIUM NITRATE, $Ca(NO_3)_2 \cdot 4H_2O$

A saturated solution of calcium nitrate at 20° has a vapor pressure about equal to a column of mercury 6.5 mm. in height, while the average aqueous pressure of air at the same temperature is about 12 mm. Consequently, the conditions are favorable to deliquescence.

Break up about 100 g. of marble into small pieces and cover them with 250 cc. of water in an evaporating dish. Heat gently and add nitric acid a little at a time until energetic effervescence ceases. Boil the solution for a time, being sure that it is acid in reaction, and dilute to about 500 cc. Meanwhile, prepare some calcium hydroxide by shaking 10 g. of quicklime with water and add this to the hot solution to precipitate the hydroxides of iron, aluminum, and magnesium. The solution should be strongly alkaline at the end of this operation. Filter off the precipitate and add enough dilute nitric acid to the filtrate to make it acid in reaction. Carefully bring the solution to crystallization, noting the fact that it is very viscous and that supersaturation will very likely be encountered. Quickly pump the crystals as dry as possible from mother liquor and dry them over effloresced calcium nitrate in a desiccator. Stir them from time to time until they are quite dry, sealing with paraffin. Place a few crystals on a watch glass and note how rapidly they become moist and deliquesce.

References: Friend, III (I), 87; Mellor, III, 850; Taylor and Henderson, *J. Am. Chem. Soc.*, **37**, 1688 (1915).

Additional Exercises: Calcium chloride, $CaCl_2 \cdot 6H_2O$; magnesium nitrate, $Mg(NO_3)_2 \cdot 6H_2O$.

III. PROTECTION FROM THE ACTION OF THE AIR

In crystallizing and drying salts, it must be remembered that the entire operation is usually carried out in the presence of air. The air contains three constituents that are more or less active as chemical reagents, *viz.*, oxygen, carbon dioxide, and water vapor, and in many cases special precautions must be taken to protect the preparation from atmospheric action. Each case will suggest a somewhat different mode of procedure, and a few typical examples will be used to illustrate these.

1. Protection from Oxidation.—The most common case of oxidation among inorganic compounds occurs with salts in which the metal has two stages of oxidation and tends to pass from the lower to the higher as a result of atmospheric oxidation. The salts of iron, copper, tin, mercury, and chromium are examples. In other cases, the acid radical tends to undergo oxidation, as is true with sulfides, sulfites, phosphites, and nitrites.

EXERCISE 8. FERROUS SULFATE, $FeSO_4 \cdot 7H_2O$

Ferrous sulfate may be taken as an example of a salt which is not very easily oxidized, so that elaborate precautions are not necessary. Its ease of oxidation is apparently influenced by the presence of catalysts, so that preparations from different materials vary in ease of oxidation. Different anions also influence the speed of oxidation of ferrous salts.

Pour 50 cc. of concentrated sulfuric acid slowly into about 1 liter of water in an evaporating dish and add 50 g. of iron nails or turnings. When the action becomes slow heat the dish until the acid is practically all neutralized, as indicated by the fact that evolution of hydrogen ceases. Filter from the undissolved iron, carbon, silicon, and other residues, using a folded filter, and evaporate to crystallization. If the solution oxidizes appreciably in the operation additional iron and acid must be added to effect reduction. Oxidation will be indicated by a change in color from bottle green to a yellowish shade of green, or by the formation of a rusty precipitate.

The salt tends to crystallize in the form of large crystal masses made up of a great number of small crystals, and these are easily crushed between the fingers. This is particularly true if the solution is strongly acid. It is useless to attempt to preserve the salt in this form since mother liquor is sure to be inclosed between the small crystals and oxidation will take place. Conditions must be sought under which the crystals form in transparent individuals, resembling bits of broken green glass. They should not be too large nor form too slowly from dilute solutions. Seeding with finely powdered crystals will be of assistance. When satisfactory crystals have been secured, they should be drained on the bare Witte plate, quickly washed with a little cold water and spread on absorbent paper to dry. It is well to put them in a warm place, as in bright sunshine, but if they become too warm they will effloresce. When they are entirely dry, seal them in a bottle with paraffin. If they are perfectly dry they are stable in the air, but if moist, they will gradually pass into a basic ferric salt.

Reference: Stability in air, De Forcrand, *Compt. rend.*, **158**, 20 (1914); *C. A.*, **8**, 1245 (1914).

EXERCISE 9. FERROUS CHLORIDE, $FeCl_2 \cdot 4H_2O$

This salt is much more difficult to obtain in dry, pure form than is the corresponding sulfate. It is very soluble in water, but from concentrated solution it is deposited in crystals which in color are almost identical with those of the sulfate. Upon exposure to air, even during filtration with the pump, the crystals turn yellow through oxidation. Probably this is not due to greater ease of oxidation on the part of the solid salt but to the physical conditions that prevail. The saturated, cold solution is very viscous and sticky, and absorbent paper absorbs this liquid very slowly. Owing to the great solubility of the salt, the solution has a low vapor pressure and does not tend to evaporate in the air. Consequently, the crystals remain coated with a film of concentrated mother liquor which oxidizes very fast in the air.

The logical way to meet this situation is to wash the crystals with some liquid that will dissolve the film and leave them clean and bright. Evidently, ferrous chloride will have to be soluble in this liquid, but its solubility should be rather small, so that the solution left upon the crystals will not be viscous and will dry rapidly. An alternative plan is to dilute the original solution with a solvent that will diminish the solubility of ferrous chloride and thus avoid some of the difficulties. Alcohol will serve this latter purpose, but it increases the solubility of oxygen in the solution, and this promotes oxidation. A better liquid is concentrated hydrochloric acid. This suggests the following procedure:

Dilute about 100 cc. of commercial hydrochloric acid with an equal volume of water in a dish of suitable size. Add iron nails from time to time and, when the action becomes slow, heat the dish until nearly all of the acid has become neutralized, as will be evidenced by the feeble evolution of hydrogen. Evaporate to about 75 cc., allow the solution partially to cool, and add 25 cc. of pure, concentrated hydrochloric acid. If no crystals form by morning, evaporate to about 50 cc., again add 25 cc. of concentrated acid, and once more set aside for crystallization. The solution will be yellowish brown in color. (Does this color necessarily indicate oxidation?) It is absolutely necessary to obtain the crystals in good form before attempting to dry them, and this may require a number of recrystallizations. Save the mother liquors after each attempt, combining them with the crystals if the process of drying is not successful and reducing with iron and hydrochloric acid when oxidation takes place. The crystals must not be too small; must be of fairly uniform size, with no fine material mixed with them; and must have clear, transparent faces.

When satisfactory crystals have been obtained, bring them quickly upon a Witte plate, washing them on with the mother liquor. Wash the crystals with successive small portions of concentrated hydrochloric acid, being careful that none escapes the washing. Pump off the liquid each time, then spread the crystals upon absorbent paper, press them lightly with a wad of absorbent paper, and transfer them to a desiccator over sulfuric acid. As soon as they are dry, put them in a perfectly dry bottle and seal with paraffin, since they are deliquescent. They should be bright green in color and not at all yellow. It is very hard to get a perfect specimen, but it can be done, and, when successful, the specimen will keep indefinitely.

Reference: Friend, IX (II), 92.

Additional Exercises: Chromous acetate, $Cr(C_2H_3O_2)_2$; chromous sulfate, $CrSO_4 \cdot 7H_2O$; chromous chloride, $CrCl_2 \cdot 4H_2O$; Anderson and Riffe, *J. Ind. Eng. Chem.*, **8**, 24 (1916); Recoura, *Ann. Chim. Phys.*, (6) **10**, 6 (1887).

EXERCISE 10. CUPROUS CHLORIDE, CuCl

In preparing cuprous chloride, it is not practicable to dry the salt in the usual way because of the rapidity of oxidation. The salt is not oxidized very rapidly when covered with water (best containing some sulfur dioxide), since it is insoluble, and oxygen must be conveyed to it through solution in water, which is a slow process. But when exposed to air in moist condition, the compound oxidizes very rapidly. In such cases, it is best to displace the water by some other liquid without allowing the salt to come into direct contact with the air; and when the water has been displaced, the other liquid is removed by evaporation. Evidently, a liquid must be chosen which is itself anhydrous; which is soluble in water; which does not readily dissolve oxygen; which will not act upon the preparation; and which is easily evaporated. In many such cases, the salt is first washed with alcohol and then with ether. This combination is not well suited to the case in hand, because both of these liquids are hard to obtain in anhydrous form; they both dissolve oxygen very readily; and they are neutral, which rather favors oxidation. Glacial acetic acid serves much better, meeting all the requirements that have been mentioned and, in addition, dissolving any basic salt arising from oxidation or hydrolysis.

The general scheme of preparation is to treat any cupric salt in solution (cupric ion) with concentrated hydrochloric acid and a reducing agent, preferably metallic copper. Powder about 50 g. of crystallized copper sulfate (the material prepared in Exercise 3) and place it in a 500-cc. round-bottomed flask together with 25 g. of sodium chloride and 150 cc. of concentrated (commercial) hydrochloric acid. Add about 100 g. of copper, if possible, in such a form as to have a large surface and to extend throughout the liquid. Heat to boiling, keeping the flask partially closed by placing a small funnel in its open mouth. Shake well from time to time and renew the acid lost by evaporation. If the solution is kept strongly acid, the heating maintained vigorously, and the copper distributed all through the liquid, the nearly black color which develops after short heating will give place to a straw yellow, and the solution will become quite transparent. If all of these conditions are not met, the solution will remain dark colored. This is because some oxidation takes place all the time, and a balance is reached between the rate of oxidation and that of reduction. In this case the yield will be decreased and the product may be discolored.

Pour the hot solution into at least 2 l. of cold water to which a few grams of sodium sulfite has been added and allow the white crystalline powder to settle. The water should contain a little sodium sulfite or sulfur dioxide, which will tend to prevent oxidation. Wash the precipitate several times by decantation, the wash water in each case containing sulfur dioxide and made acid with hydrochloric acid. Finally, collect the precipitate on a small Witte plate provided with a close-fitting filter paper, washing it on to the plate with portions of the filtrate and taking care not to let all the liquid drain through the filter, exposing the moist compound to the air.

Have at hand 50 cc. of glacial acetic acid. Turn on the pump, and when the water just sucks through the cake of precipitate, stop the pump and at once pour over the precipitate about 10 cc. of the acid, carefully plugging up all drainage channels with a spatula. Let the acid percolate slowly through the preparation, and after a few minutes suck it through and repeat the operation with a new portion of glacial acetic acid. When all the acid has been used, pump the material as dry as possible, remove it from the paper with a spatula, and place it in a porcelain dish to dry on the hot plate or in an air oven at about 125°. When completely dry, bottle the preparation and seal it with paraffin. It should be snow white and is entirely stable if prepared properly. The salt dissolves in hot concentrated hydrochloric acid, from which it may be crystallized in colorless cubes.

References: Friend, II, 261; Mellor, III, 157; Lupton, *Chem. News*, **30,** 233 (1874); Rosenfeld, *Ber.*, **12,** 954 (1879).

Topics: Cuprous salts of oxygen acids, Daniels, *J. Am. Chem. Soc.*, **37,** 1167 (1915); Sloan, *ibid.*, **32,** 972 (1910).

Additional Exercises: Cuprous sulfite, Cu_2SO_3, Groger, *Z. anorg. Chem.*, **28,** 154 (1901).

Alternative Method.—Cupric chloride would serve better than a mixture of salt and copper sulfate, but it is much more expensive. A still simpler way is to start with copper. Place a suitable quantity in a flask and add concentrated hydrochloric acid in the ratio given in the last exercise. Heat nearly to boiling and add concentrated nitric acid drop by drop through a separatory funnel. When most of the copper has dissolved, stop adding nitric acid, heat vigorously for a time, and pour into cold water containing sodium sulfite. Proceed as in the first method. The aqua regia converts some of the copper into cupric chloride, and this is reduced to the cuprous salt by the excess of copper.

Reference: Jones, *Am. Chem. J.*, **22,** 288 (1899).

2. Protection from Carbon Dioxide.—In working with substances in alkaline solutions, it is sometimes necessary to protect the solution from the carbon dioxide in the air. This is particularly true when compounds are present that can form insoluble carbonates. In all such cases, the operations involved must be carried out in closed vessels containing air that has been purified by drawing it over a suitable absorbent such as soda lime. When this is not practicable, it is better to work in the open air rather than in the laboratory.

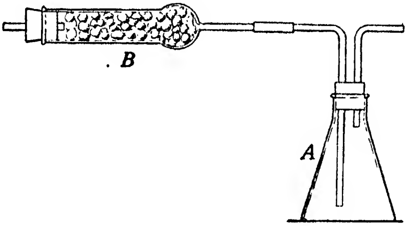


Fig. 3.

EXERCISE 11. CRYSTALLIZED BARIUM HYDROXIDE, $Ba(OH)_2 \cdot 8H_2O$

Prepare a hot solution of 100 g. of commercial barium chloride in 200 cc. of water in an Erlenmeyer flask. Add a solution of 30 g. of sodium hydroxide in 30 cc. of water and set the flask aside for crystallization. When cold, decant off the mother liquor as completely as possible and dissolve the crystals in as little hot water as will suffice. The solution will be turbid from suspended barium carbonate and must be filtered into a vessel containing purified air. Proceed as follows: Secure an Erlenmeyer flask of about 500 cc. capacity and fit it with a two-hole stopper, carrying a right-angled tube that reaches to near the bottom of the flask (Fig. 3). Through the other hole insert a short right-angled tube so that the end extends just through the stopper. Fill a good-sized calcium chloride tube with equal parts of granular calcium chloride and soda lime and attach this to the long tube. Connect the short tube with the water pump and draw air through the flask for a time. Remove the long tube from the stopper and replace it with the stem of a funnel (Fig. 4), without removing the stopper from the flask. Fit the funnel with a carefully folded filter paper, which has been wet with water, and press it snugly into place. Pour the hot solution upon the funnel and allow it to filter into the flask containing purified air. As soon as the filtration is complete, remove the funnel and plug the hole with a bit of glass rod. Disconnect the pump, connect the calcium chloride tube with the short right-angled tube, and set the flask aside for crystallization.

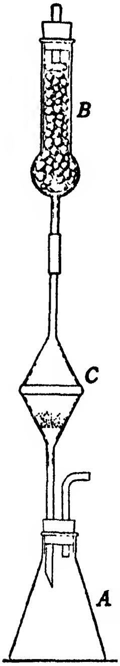


Fig. 4.

Obtain two funnels the rims of which are of just the same size. Provide one of them with a stopper which fits your filter flask and also with a Witte plate. Attach the calcium chloride drying tube to the stem of the other. Provide also a piece of rubber tape such as is used to wrap joints in electrical wires and long enough to reach around the rim of the funnels and lap over for a joint.

Shake the flask containing the crystals until any cake that may have formed is broken up and quickly pour the contents of the flask onto the Witte plate. Place the second funnel rim to rim with the first as a cover and bind the rubber tape around the joint to hold the two together by an airtight joint. Pump off the mother liquor and continue to pump air through the flask until the crystals are nearly dry. Quickly transfer the crystal mass to a desiccator containing effloresced barium hydroxide and finish the drying over this reagent. When dry, the crystals do not absorb carbon dioxide very rapidly, but they should be securely bottled.

References: Friend, III (I), 218; Mellor, III, 675.

Additional Exercises: Strontium hydroxide, $Sr(OH)_2 \cdot 8H_2O$.

Topics: Law of mass action; solubility product; Mellor, I, 300, 494, 996; textbooks on physical chemistry.

3. Protection from Moisture.—The moisture in the air may act upon chemical preparations in a variety of ways. (1) It may combine with the preparation to form an entirely different compound, as when calcium oxide is converted into the hydroxide. (2) With very soluble salts it may occasion deliquescence (see Exercise 7). (3) It may occasion hydrolysis. This last case may best be considered in connection with hydrolysis in solution, since the causes underlying each are the same.

Hydrolysis.—A salt that contains as one of its constituents either a weak acid or a weak base will not dissolve in water to form a neutral solution. Water acts upon such a salt partially to reverse the reaction of neutralization, liberating equivalent parts of both acid and base. To obtain in solid form a normal salt that is subject to hydrolysis, it is necessary to have present in the solution considerable excess of either the acid or the base, depending upon the nature of the salt; and the mother liquor from which the salt is crystallized will contain this excess. When the crystals have been drained from this mother liquor, they cannot be washed with the pure solvent, for this would leave them coated with a film of the aqueous solution of the normal salt, which would then undergo hydrolysis. If either the acid or the base of which the salt is composed should be difficultly soluble, a precipitate may form on the crystals as a result of an attempt to wash them, or a difficultly soluble basic salt may form. Moreover, if the salt is very soluble, the crystals will be deliquescent, and when they are exposed to moist air they will attract moisture from the air and hydrolyze in the resulting solution. The proper mode of procedure will depend upon the characteristics of the individual salt. Two examples will be described.

References: Friend, I, 227; Mellor, I, 1009; textbooks on physical chemistry.

EXERCISE 12. FERRIC NITRATE, $Fe(NO_3)_3 \cdot 9H_2O$

To a mixture of 100 cc. of concentrated nitric acid and 30 cc. of water, add 50 g. of iron filings or fine turnings in small portions at a time, shaking or stirring the mixture frequently. The rate of reaction can be regulated by the rate of addition of iron and by gently heating the mixture but not above 70°. If large pieces of iron (nails) are used, the iron is likely to become "passive," and action is difficult to maintain and regulate.

When the iron has practically all dissolved, filter the solution through an asbestos mat and set it aside to crystallize. The filtrate is usually dark in color owing to the presence of colloidal basic nitrates. These salts are gradually converted into the normal nitrate, and the color becomes very much lighter. The filtrate is markedly viscous, and supersaturation is the usual thing, so it is almost always necessary to add a seed crystal. If no crystals form after standing for a day or so and then seeding, evaporate at a gentle heat but do not boil. Since the crystals are somewhat less soluble in concentrated nitric acid than in water, the addition of full-strength acid will sometimes bring a solution to crystallization. If the crystals form a cake, the solution can be diluted with nitric acid to which three parts of water has been added.

When well-formed individual crystals have been obtained, filter them on a Witte plate, wash once with dilute nitric acid (1:3), pump as dry as possible, place the moist crystals in a suitable vessel, and put this in a desiccator over sulfuric acid. Watch the crystals carefully, with occasional stirring, and bottle them at once when they are dry. Do not touch them with the fingers, as this will discolor them. If they are allowed to overdry in the desiccator, they lose both crystal water and nitric acid and turn into a sticky mass of brownish-colored basic salt, which will not take up water from the air to reverse the reaction. Consequently, effloresced crystals cannot be used to complete the drying of the moist crystals. If the crystals are exposed to moist air, they deliquesce, undergo hydrolysis in the resulting solution, and form a basic salt. If they are bottled before they are dry, they will in time become discolored. If properly prepared, they will remain perfectly transparent and have a very pretty amethyst color, the intensity of which depends upon the size of the crystals. Crystals of iron alum have the same color.

There has been much discussion as to whether the color is a property of the pure crystals or is due to an impurity (manganese). Under certain conditions, a salt of the formula $Fe(NO_3)_3 \cdot 6H_2O$ is obtained, temperature and acidity being the determining factors. An acid salt is also known.

References: Friend, IX (II), 176; Divers, *J. Soc. Chem. Ind.*, **23**, 1182 (1904); Montemartini, *Gazz. chim. ital.*, **22**, 253 (1892); Cameron and Robinson, *J. Phys. Chem.*, **13**, 251 (1909); Transition of the 9-hydrate to the 6-hydrate, Malquori, *Atti accad. Lincei* (6), **9**, 324 (1929); Passive iron, Byers, *J. Am. Chem. Soc.*, **30**, 1718 (1908); Ephraim, p. 103.

Additional Exercises: Bismuth nitrate, $Bi(NO_3)_3 \cdot 5H_2O$; aluminum nitrate, $Al(NO_3)_3 \cdot 18H_2O$; trisodium phosphate, $Na_3PO_4 \cdot 12H_2O$.

EXERCISE 13. ANTIMONY SULFATE, $Sb_2(SO_4)_3$

Like ferric nitrate, antimony sulfate is decomposed by water, various basic salts being formed, the simplest of which has the formula $(SbO)_2SO_4$. The normal salt is stable only in rather concentrated sulfuric acid. Since this latter solvent has almost no vapor pressure at ordinary temperatures, the moist salt cannot be dried by evaporation of the solvent. It cannot be dried on absorbent paper, since the oily liquid rapidly carbonizes it. In such a case, it is best to take advantage of the drying qualities of unglazed earthenware (porous plate), such as the "biscuit" which forms the body of dishes. Owing to the fine pores which this material contains, liquids are sucked up by it by capillary attraction, and it is not acted upon by most reagents.

Powder very finely 20 g. of antimony oxide, Sb_2O_3 (or metallic antimony), and add this in small portions at a time to 250 cc. of hot concentrated sulfuric acid contained in an evaporating dish. Maintain the heat until all of the powder has been dissolved, if necessary adding a little more acid to keep the white sulfate in solution. Allow the solution to cool and filter off the fine crystals on a platinum cone or a Witte plate with very small holes, pumping them as dry as possible. Spread the pasty mass on pieces of unglazed dishes, putting one such piece on top of another, to make a pile that consists of alternate layers of plate and sulfate. Put the entire pile in a desiccator so as to prevent absorption of moisture from the air. If the sulfate is rather wet, it may be necessary to scrape it off the plates and repeat the operation with fresh ones. Finally, spread the preparation on a clean, dry plate and allow it to become completely dry. If it is desired to remove the last traces of sulfuric acid, the preparation may be washed with xylene.

References: Mellor, IX, 580, Metzl, *Z. anorg. Chem.*, **48**, 143 (1906); Adie, *J. Chem. Soc.*, **57**, 540 (1890).

Topic: Basic salts, Mellor, I, 394; Friend, I, 199.

Additional Exercises: Mercurous sulfate, Hg_2SO_4, Baskerville and Miller, *J. Am. Chem. Soc.*, **19**, 873 (1897); Bismuth sulfate, $Bi_2(SO_4)_3$, Allen, *Am. Chem. J.*, **27**, 284 (1902).

IV. DOUBLE DECOMPOSITION

The method of preparing salts by double decomposition can be employed in so many cases that it is important to understand thoroughly the principles involved in the procedure and to acquire skill in the necessary manipulation.

In general, when two salts are brought together in solution, a new simple salt, resulting from double decomposition, may crystallize from the solution; or a double salt, a complex salt, or a solid solution may be formed. The first case only will be considered at this time, others being deferred to later exercises.

When two salts are brought together in solution, we may suppose that the various ions are free to unite in all possible combinations. That particular combination will precipitate, or will crystallize first as the solution is evaporated, whose solubility product is first exceeded. By the solubility product of a salt is meant the number obtained by multiplying the concentration of the cation by the concentration of the anion, both being measured in a *saturated solution* of the salt and expressed in terms of gram ions per liter.

$$C_{(\text{cation})} \times C_{(\text{anion})} = K = \text{solubility product.}$$

For example, a saturated solution of calcium sulfate at 25° contains 2.08 g. $CaSO_4$ in 1 l. of solution. In terms of gram molecules per liter, the concentration is $2.08/136.13 = 0.0153$. In a solution as dilute as this, the salt may be considered to be very largely ionized. If it is assumed that it is completely ionized (or determining its percentage of ionization at this concentration and making corrections), the gram-ion concentration of each ion is 0.0153. The solubility product K is therefore $= 0.0153 \times 0.0153 = 0.000234$. When calcium ions from any source are brought into the presence of sulfate ions from any source, calcium sulfate will precipitate until the product of the concentrations of these two ions remaining in the solution falls to the value 0.000234.

When the solubility product of the least soluble combination is fairly large, only a small fraction of the ions (or none at all) will leave the solution as solid salt. It must be remembered also that the solubility of salts changes rapidly with change in temperature, and obviously the solubility product will change in the same way. Consequently, two salts may produce no precipitate when brought together in hot solution, but the double-decomposition product may crystallize out on cooling, because its solubility product has decreased more rapidly than that of either of the salts originally brought together

Applications.—Three general applications may be made of these principles: (1) A desired salt of small solubility product (small solubility) may be obtained by precipitation. (2) By properly choosing salts, a salt not desired may be precipitated, leaving the desired soluble salt (large solubility product) in solution. The latter may then be recovered by evaporation and crystallization. (3) Two soluble salts may be brought together in solution, and a double-decomposition product may crystallize on cooling. In the last case, the yield may fall far below that of a quantitative reaction. As an example, refer to the preparation of barium hydroxide (Exercise 11). An additional example is the preparation of KNO_3 by cooling a solution of $KCl + NaNO_3$ saturated with each salt at the boiling point.

References: Textbooks on advanced general chemistry or on physical chemistry; Stieglitz, Qualitative Chemical Analysis, Part I, p. 139 (1925).

EXERCISE 14. CALCIUM CARBONATE, $CaCO_3$

Application 1.—The solubility of calcium carbonate at 180 is 14 mg. per liter. The solubility product of the salt is therefore very small (calculate this).

First prepare a pure solution of calcium chloride by following the directions for the preparation of calcium nitrate in Exercise 7 but substituting hydrochloric acid for nitric acid and using 100 g. of marble. Do not add the excess of acid at the end of the operation but leave the solution strongly alkaline. It is also well to add about 10 cc. of bromine water to the acid solution while boiling it and before the addition of the slaked lime. This is to oxidize any ferrous salts that may be present.

Meanwhile, prepare a solution of ammonium carbonate as follows: Break up 90 g. of commercial ammonium carbonate into small pieces and dissolve it in 1 l. of cold water to which has been added about 30 cc. of concentrated ammonia. *The solution should not be heated,* for this will decompose the ammonium carbonate, but solution will be greatly hastened by stirring or shaking. Pour the solution of calcium chloride into the ammonium carbonate slowly and with constant stirring. Place the dish on the hot plate and allow the precipitate to settle. Decant the mother liquor as completely as possible, saving it for later use. In a similar way, wash the precipitate several times by decantation, adding the first wash water to the original mother liquor. Either of two impurities may be present, *viz*, excess of ammonium carbonate or ammonium chloride. Of these, the latter is the more abundant, and when it has been washed out it may be assumed that the carbonate is no longer present. The precipitated calcium carbonate should now be collected on a Büchner funnel and washed until the filtrate no longer gives a test for the chlorine ion with silver nitrate. (Be sure to add nitric acid to the sample of the filtrate before adding the silver nitrate. Why?) Finally, pump the precipitate as dry as possible and complete the drying on the hot plate.

The mother liquor saved from the precipitate should be evaporated to recover the ammonium chloride which it contains. If it is not clear, it should be filtered, and hydrochloric acid should then be added to neutralize the ammonia and decompose the ammonium carbonate. Having made the solution decidedly acid, evaporate to crystallization, securing a second crop of crystals if the first crop is small. The final mother liquors should be rejected, as they will contain ammonium bromide.

References: Friend, III (I), 108; Mellor, III, 818.

Additional Exercises: Lead chromate, $PbCrO_4$; calcium phosphate, $Ca_3(PO_4)_2$; ferrous oxalate, $Fe(C_2O_4)$; sodium chloride, NaCl, precipitated from a saturated solution by HCl gas, Richards and Wells, Revision of the atomic weights of sodium and chlorine, *J. Am. Chem. Soc.*, **27**, 459 (1905).

EXERCISE 15. CUPRIC CHLORIDE, $CuCl_2 \cdot 2H_2O$

Application 2.—The second plan of procedure is well illustrated in the preparation of cupric chloride, which is very soluble in water. The cheapest salt of copper is the sulfate, and this may be brought into double decomposition with the chloride of any metal whose sulfate is practically insoluble. Barium is the ideal metal, since its sulfate is so highly insoluble. However, barium chloride is rather expensive, and calcium chloride will serve fairly well instead. By its use a number of complications result. Calcium sulfate has a very appreciable solubility in water (about 2 g. per liter at room temperature), and in concentrated salt solutions its solubility is very much greater. Consequently, if a dilute solution of copper chloride is saturated with calcium sulfate and the solution is then evaporated, the increasing concentration of the copper chloride keeps the calcium sulfate in solution, and not much separates as a precipitate during evaporation. This situation affords an opportunity for the exercise of some ingenuity.

Dissolve 250 g. of copper sulfate free from iron (use the material prepared in Exercise 3) in 1.5 l. of water and heat to boiling. A solution of calcium chloride must now be added in such a quantity as to enter into exact double decomposition with the copper sulfate. The weight of calcium chloride can be calculated easily, but the salt cannot be weighed out with precision. The anhydrous salt used as a drying reagent contains a variable percentage of both water and calcium oxide. The hydrated salt is not available as a rule and is too deliquescent for exact weighing. Either of two courses can be followed: (1) Calculate the weight of pure calcium carbonate equivalent to the 250 g. of hydrated copper sulfate. With care, weigh out this quantity to decigrams, using the material prepared in Exercise 14. Suspend it in about 200 cc. of water and add concentrated hydrochloric acid a little at a time until it is all dissolved. Boil to expel the carbon dioxide and to decompose the acid carbonate and add the solution slowly to the hot solution of copper sulfate. (2) Dissolve 120 g. of anhydrous calcium chloride in 500 cc. of water and heat the solution to boiling, adding about 10 cc. of hydrochloric acid. Pour about four fifths of the latter solution into the solution of copper sulfate and allow the precipitate to settle. Then, with greater care, add more of the calcium chloride until a further addition fails to give a precipitate. Since it is easy to go beyond this point, it is well to save out a little copper sulfate and use this to come back to a more perfect end point. When near the end point, it is also well to filter off a little of the solution and make the test with the filtrate rather than to add more reagent to the main solution. By adding alternate portions of the two solutions, almost perfect double decomposition can be secured. At the end, it is better to have a little copper sulfate in excess than calcium chloride.

After either procedure, filter off the calcium sulfate on a Büchner funnel. It should be washed until it is pure white, air dried, and preserved as a specimen, but the wash water should not be added to the main filtrate. It will be found that it will filter better if it is digested overnight on the hot plate, for a precipitated powder always tends to grow into somewhat coarser crystals on long warming in the mother liquor. (Why is this?)

Evaporate the filtrate containing the copper chloride, noting that, as evaporation proceeds, the solution gradually becomes filled with silky crystals of calcium sulfate. Continue the evaporation to dryness and extract the very soluble copper chloride by adding about 100 cc. of warm water, stirring for a moment, and decanting from the mass of calcium sulfate. Do not filter, for solutions of copper chloride dissolve filter paper. If necessary, wash with a second small portion of water. Bring the solution of copper chloride to crystallization and, if more calcium sulfate should separate, repeat the evaporation to dryness and the extraction with water. Copper chloride usually crystallizes in a mass of fine needles or pearly scales, and it is difficult to get it into the form of individual crystals. Filter off the crystalline mass on a Witte plate, pumping it as dry as possible from mother liquor, while pressing the crystals upon the plate with a spatula. Dry on a porous plate and transfer to a desiccator over calcium chloride, breaking up all lumps of crystals. When dry, the product should be a pale robin's-egg blue in color. If it remains green and refuses to dry properly, it is probable that it is contaminated with calcium chloride that has been added in excess. If sapphire-blue, transparent crystals are obtained, they are copper sulfate, and not enough calcium chloride was added. In either case, the salt must be dissolved, and the double decomposition must be completed with more care.

References: Mellor, III, 168; Friend, II, 273.

Topic: Solubility of calcium sulfate in salt solutions, Cameron and Brown, *J. Phys. Chem.*, **9**, 210 (1905); Cameron and Bell, *ibid.*, **10**, 210 (1906).

Additional Exercises: Ferrous nitrate, $Fe(NO_3)_2 \cdot 6H_2O$ (difficult), Fink, *Z. anorg. Chem.*, **20**, 404 (1899).

EXERCISE 16. CRYSTALLIZED BARIUM THIOSULFATE, $BaS_2O_3 \cdot H_2O$

Sometimes it is desired to obtain a small quantity of a sparingly soluble salt in well-crystallized condition rather than in the form of a fine precipitate. This may be accomplished by allowing the double decomposition to proceed slowly by *diffusion.*

Obtain a large beaker of at least 2 l. capacity or a battery jar or a rather deep crystallizing dish of about 25 cm. diameter, also two small crystallizing dishes (or beakers without lips) of about 75 cc. capacity (Fig. 5). Fill the one small dish three fourths full with a saturated solution of sodium thiosulfate, adding some crystals of the solid salt. Similarly, add to the second dish a saturated solution and crystals of barium chloride or nitrate. Place the two dishes 3 or 4 cm. apart in the large dish and carefully fill them with water without stirring. By means of a rubber tube connected with the supply of distilled water, flow water into the large vessel to a height of at least 4 cm. above the tops of the small beakers. The whole idea is to avoid the premature mixing of the two reagents. Pour a layer of melted paraffin over the surface of the water to protect the contents of the vessel from disturbances that might produce convection currents and set the vessel away in a place where it can remain undisturbed for several weeks at as nearly constant temperature as possible.

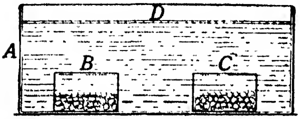


FIG. 5.—Diffusion crystallization.

The crystals form very slowly, as diffusion brings the reagents into contact. When a sufficient crop has been secured, carefully remove the paraffin, siphon off the solution as well as possible, and lift out the small beakers with their contents. Collect the crystals and dry them on paper. The place where they will form will depend on the relative rates of diffusion of the two ions concerned in the precipitation.

References: Johnston, *J. Am. Chem. Soc.*, **36,** 16 (1914); Fernelius and Detling, *J. Chem. Educ.*, **11,** 176 (1934).

Additional Exercises: Calcium hydroxide from sodium hydroxide and calcium chloride; silver nitrite from silver nitrate and sodium nitrite; manganese sulfite, $MnSO_3 \cdot 3H_2O$, from manganese chloride and sodium sulfite (adding a little SO_2 to the solution); mercuric iodide from potassium iodide and mercuric chloride.

V. DISTILLATION

A liquid which has a vapor pressure of as much as 760 mm. of mercury at any temperature which permits the use of a suitable container may be purified from nonvolatile impurities by the process of distillation at atmospheric pressure. By working under reduced pressure, the vapor pressure of the liquid need not be nearly so great as 760 mm. As a rule, a liquid may also be separated from other liquids provided the vapor pressures of the two differ enough to cause them to boil at considerably different temperatures. To effect complete separation, the process of distillation must be repeated a number of times in a systematic way and is then called fractional distillation.

While distillation finds constant application among organic compounds, its employment is more limited in inorganic chemistry. Apart from water and a few important acids, the most familiar types of inorganic liquids are the halogen compounds of the acid-forming elements, and applications of the process of distillation to these liquids will be found in later exercises. Some metals can be distilled with no great difficulty, especially under diminished pressure; and by working at low temperatures, we can distill some of the oxides of acid-forming elements with great ease.

Reference on Distillation: Mellor, I, 553, 437; any textbook on physical chemistry.

EXERCISE 17. THE DISTILLATION OF MERCURY

The chief contamination of carefully filtered mercury is dissolved metals, notably copper, zinc, cadmium, lead, gold, or silver. The last two will not be present in more than traces unless the mercury has been used for certain experimental purposes. Experiment has shown that in an ordinary distilling operation, all of these metals will distill along with the mercury, though the amount of gold or silver in the distillate will be very small and will disappear on second distillation. But if a slow current of air is drawn through the vessel during distillation, the vapors of all the base metals are oxidized, and only mercury (with traces of gold and silver) passes into the distillate. These facts have suggested a form of apparatus that can be made by anyone possessing even a moderate degree of skill in the manipulation of glass.

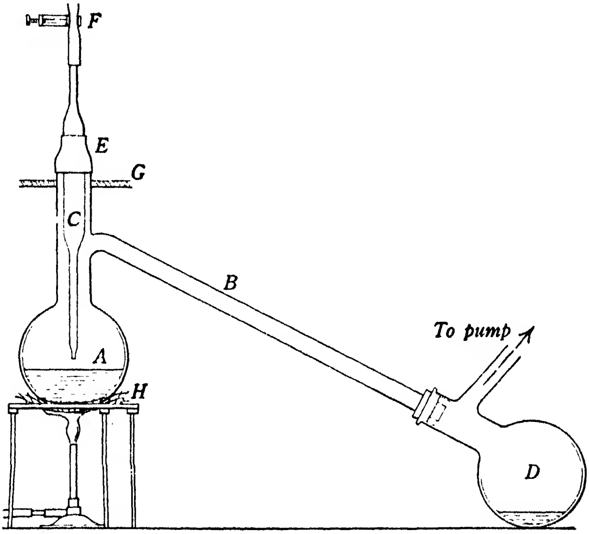


Fig. 6.—Distillation of mercury.

Select a 250-cc. distilling flask *A* (Fig. 6) with a long neck and with the side tube as near the bulb as possible. Cut off the flare of the neck so as to leave the neck cylindrical to the very end. This is easily done as follows: At one end of a piece of heavy iron wire (telegraph wire), make a half circle a little larger in diameter than the tube to be cut off and clamp the wire in a horizontal position, loop down. Make a sharp file scratch in the neck of the flask at the point just before the flare begins. Heat the loop as hot as possible with a burner; then remove the flame and at once lay the neck of the flask in the hot loop and rotate the glass so as to heat the neck in a circle through the file mark. The glass will break in a clean circle, and the sharp edge is removed by a file.

Cut off the delivery tube at a distance of about 1.5 cm. from the neck and seal on a tube *B* of thin glass 1.3 cm. in diameter and 50 cm. to act as an air condenser, bending the tube as shown in the figure. Make a tube *C* shaped like a pipette the wide part of which will just slip into the neck of the flask. The lower end is of very small tubing drawn to a capillary at the tip. When the tip is almost at the bottom of the flask, the upper part of the narrow tube should be just above the outlet into the condenser tube. The wide tube should extend about 3 cm. above the end of the neck of the flask and should then contract to a short, narrow tube over which a short piece of rubber tubing, provided with a pinch cock *F*, is slipped.

The far end of the condenser tube is passed through a stopper fitting a small distilling flask *D*. The delivery tube of *D* is connected with a manometer and a water pump.

Obtain a hemispherical iron dish *H*, somewhat larger than the bulb of the flask, and place enough fine sand in it to make contact with the glass flask. Place the sand bath with the flask upon a small ring support and steady the flask with a burette clamp. Put a suitable quantity of mercury in the flask and make an airtight connection at *E* by binding the joint with adhesive tape, used by electricians or surgeons. Assemble all the apparatus with tight joints. Turn on the water pump and close the pinch cock until a stream of only very fine bubbles passes through the mercury when the manometer shows a pressure of 25 to 30 mm.

Now carefully heat the mercury to boiling and distill at a slow rate. It may be necessary to fashion a shield of asbestos paper over the top of the distilling flask to diminish the radiation and prevent the mercury vapor from condensing before it reaches the outlet tube. If the upper neck of the distilling flask tends to get hot, cut a round hole in a piece of asbestos board of such size as to make a tight fit over the neck of the flask and slip it over the neck for a shield, as shown at *G*. The mercury should come over perfectly clean. If it looks at all dim, it is probably because the air pressure in the flask has not been reduced low enough.

References: Hulett, *Phys. Rev.*, **33**, 307 (1911); Friend, III (II), 203.

Additional Exercises: Preparation of a low-boiling metal such as rubidium or cesium, Graves, *J. Chem. Educ.*, **9**, 1274 (1932); Grosse, *Ber.*, **59B**, 2646 (1926).

EXERCISE 18. NITROGEN DIOXIDE, NO_2

Its Preparation and Distillation.—Place about 50 g. of arsenious oxide and 100 cc. of concentrated nitric acid in a 250-cc. flask *A* (Fig. 7), provided with a thistle tube *B* and a delivery tube. Use a cork stopper that has been dipped into water glass to protect it from the action of the oxides of nitrogen. If available, lumps of white arsenic are better than the powdered form. Thoroughly wet the oxide by rotating the flask on a sand bath (using only enough sand to make good contact with the glass) and arrange the bath at a suitable height for heating. Connect the delivery tube with one branch of a T tube, and the stem of the T tube with a train consisting of (1) an empty gas-washing flask *C*; (2) a good-sized U tube *D* loosely filled with glass wool or shredded asbestos; (3) a second empty wash flask *E*; and (4) a U tube *F* having its bend filled with glass beads or bits of broken glass tubing and set in a large beaker. Pack the U tube *F* with ice and salt in the ratio 3:1 by weight. "Dry-ice," obtainable from any dealer in ice cream, is a much more efficient freezing material. Connect the other branch of the T tube with a gas-washing flask *G*, containing sulfuric acid to a height of a few centimeters to act as a gauge, and the flask in turn with a source of *dry* air (or, better, oxygen).

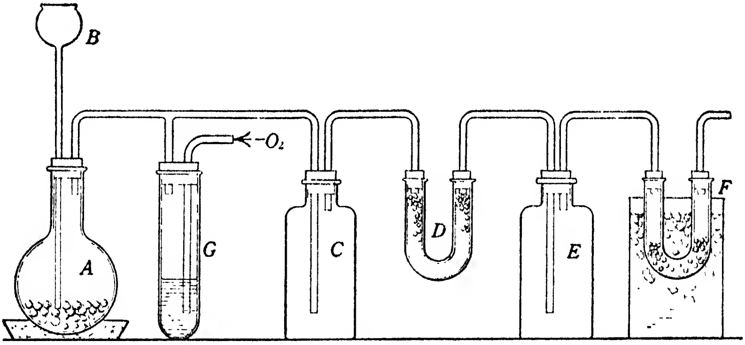


FIG. 7.—Preparation of nitrogen dioxide.

The empty wash flasks are intended to act as condensers for the moisture which comes over with the tetroxide. This gas acts upon almost all of the ordinary drying reagents, though lumps of freshly heated calcium nitrate may be used if available. In all of the connections save that with the air supply, the ends of the tubes to be joined should be brought close together, since nitrogen dioxide acts very energetically upon rubber.

If finely powdered arsenious oxide is used, the action usually proceeds rapidly enough without heat, and it may even be necessary to cool the generating flask by removing the sand bath and immersing the flask in cold water. As the action proceeds, it may be necessary to heat the flask gently.

As soon as the reaction is well started, admit a gentle current of dry air or oxygen through *G*. The nitrogen dioxide condenses in the cold U tube *F* to a yellow liquid, often colored green, blue, or dark brown by dissolved nitric oxide (which forms trioxide in the solution) and by nitric acid. The oxides of nitrogen are all changed into the dioxide by oxygen; but the current must be very slow, or much of the dioxide will be lost by volatilization. The air (or oxygen) must be dry, for water acts upon the oxides of nitrogen converting them into nitric acid. If much of the latter is formed, the liquid will split into two liquid phases, the one essentially nitric acid, the other nitrogen dioxide. These cannot be separated by fractional distillation. As the air (or oxygen) passes through the dark liquid, the color gradually changes, and the operation is complete when the color is a light amber. The solution of arsenic acid remaining in the generating flask should be preserved for use in Exercise 39.

The volatile liquid (boiling point, 22°; melting point, −10°) must now be distilled from the U tube and sealed in a glass tube. Select a strong tube of suitable diameter of soft glass, seal one end, and blow it out to rounded form like a test tube. At a height of the tube such that the volume below will be about twice that of the liquid to be preserved, soften the tube and draw it to a constriction of such diameter that the smallest tubing available will just slip into it (*A*, Fig. 8). Then cut the tube off about 3 in. beyond the constriction.

Select a piece of small tubing *B* that will just slip into the constriction and make a right-angle bend in it so that one end will reach to the bottom of the sealing tube and the other end will be about 20 cm. in length. Thoroughly dry the sealing tube and pack it in a freezing mixture in a beaker glass, leaving the open end above the pack. Insert the small tube and connect the other end to one branch of the U tube containing the dioxide, first removing the U tube from the ice in which it has been packed. Plug up the other branch of the U tube with a piece of tubing and a glass plug. The nitrogen dioxide will now distill from the U tube at room temperature into the sealing tube.

When the latter is half full, stop the process and withdraw the small glass tube from it, taking care not to wet the constriction. Bring the tube, still in the freezing bath, to the blast lamp and seal it at the constriction. This will take some skill, and it is well to try the manipulation on an empty tube or one half full of water. With one hand, hold the tube lightly below the constriction; and with the other, above. Have the flame not too large, of a bushy shape, and in a nearly horizontal position. It will be found that by holding the tube at an angle of about 45 deg. to the mouth of the beaker, it will be possible to bring the flame to play on the constriction, while keeping the lower half of the tube in the bath, and at the same time not burn the fingers. When the tube has become a little warm, turn the flame to a fine point and seal the

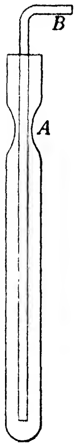


FIG. 8.—Sealing tube for volatile liquids.

tube while constantly rotating it. The tube should not be drawn apart but heated until the walls seal together and finally melt in two.

References: Friend, VI (I), 167; Mellor, VIII, 530; Hazenbach, *J. prak. Chem.*, (2) **4,** 1 (1871); Cohen and Calvert, *J. Chem. Soc.*, **71,** 1052 (1897); Ramsay and Cundall, *ibid.*, **47,** 187 (1885); Ramsay, *ibid.*, **57,** 590 (1890).

EXERCISE 19. SULFUR DIOXIDE, SO_2

In a flask similar to that employed in the preparation of nitrogen dioxide and placed on a sand bath, warm 50 g. of copper turnings and 200 g. of concentrated sulfuric acid. The rate of evolution of the gas is to be regulated by the heat supplied and not by the addition of more acid. The thistle tube acts merely as a safety tube and should dip below the surface of the acid in the flask. Bubble the sulfur dioxide through concentrated sulfuric acid contained in a gas-washing flask and then pass it into a U tube containing glass beads, as in the previous exercise, and immersed in a freezing mixture. This gas is more difficult to condense at ordinary atmospheric pressure than NO_2 and should be evolved slowly; the U tube should not be too large in diameter; and the freezing bath should be as efficient as possible. This is secured by having the ice finely powdered and intimately mixed with salt in the ratio of 3:1 by weight. If available, solid carbon dioxide ("dry ice") should be used as a freezing medium. When a sufficient quantity of the liquid has been secured, it should be distilled into a sealing tube, and the end sealed in exactly the same way as described in the last Exercise.

References: Friend, VII (II), 103; Mellor, X, 188.

VI. THE PROCESS OF SUBLIMATION

A considerable number of inorganic solids have an appreciable vapor pressure at temperatures within easy range of laboratory heating devices. Such solids may be purified from nonvolatile impurities by heating the mixture and condensing the vapors. This process is called *sublimation.* In some cases, a volatile compound may be made by heating two compounds which, by double decomposition, give the desired compound. Examples of such a procedure are found in the manufacture of mercuric chloride and ammonium carbonate. This method of synthesis is much better adapted to factory operations than to the laboratory. When the vapor condenses, it passes directly to the solid state and usually assumes the form of a very fine smoke, like that occasioned by the union of hydrogen chloride and ammonia in the laboratory atmosphere. These smokes are very hard to collect into a solid mass, the best success attending operations on the large scale where complicated and roomy condensers can be used. Methods involving the use of highly charged electrical condensers are especially effective. As a purification method, however, sublimation has a limited application even in the laboratory. The following example will illustrate a simple procedure.

References: Friend, I, 46; Cottrell, Methods of condensing smokes, *J. Ind. Eng. Chem.*, **3**, 542 (1911).

EXERCISE 20. THE PURIFICATION OF ARSENIOUS OXIDE, As_2O_3

Secure an evaporating dish of about 10 cm. diameter and support it on a ring stand at a convenient height for heating. Provide a funnel the bell of which is somewhat smaller in diameter than the dish, so that when it is inverted in the dish it will act as a cover resting upon the sloping sides of the dish (Fig. 9). Slip the stem of the funnel through one hole of a two-holed stopper, which fits the neck of a 500-cc. Erlenmeyer flask. Join the flask to the stopper and clamp it in an inverted position. Place about 30 g. of arsenious oxide (white arsenic) in the dish, fit the funnel closely to the dish, and apply a gentle heat to the dish, increasing the heat until fumes are seen to be arising from the arsenic and condensing on the funnel (Hood). Continue the heating until all of the arsenic has been volatilized. After the apparatus has cooled, scrape the crystalline oxide from the sides of the funnel. Wash the various vessels in dilute alkali to remove the arsenic and remember in handling it that it is very poisonous. Very little of the subliming material will make its way up through the stem of the funnel into the flask; and if the work is conducted in a good hood, the flask can be dispensed with.

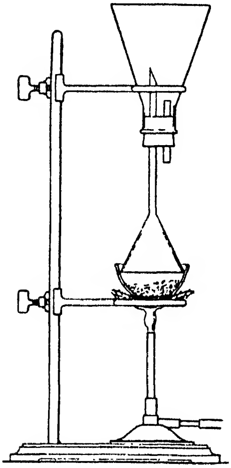


FIG. 9.—Sublimation of arsenious oxide.

References: Mellor, IX, 90; Read, *J. Ind. Eng. Chem.*, **20,** 97(1928).
Additional Exercises: Purification of iodine; preparation of ammonium carbonate from calcium carbonate and ammonium chloride; mercuric chloride from mercuric sulfate and sodium chloride.

VII. FURNACE METHODS

In the preparation of many compounds, it is necessary to heat the ingredients to a high temperature, sometimes to the point of fusion. On a small laboratory scale, this is usually accomplished by a Roessler or Fletcher furnace, though many laboratories are equipped with electric furnaces. The usual size of the gas furnaces will hold a Hessian crucible, about 5 in. high and 4 in diameter. They are lined with fire clay and heated by a gas flame disposed so as to give the greatest heating effect. The Roessler furnace is heated by a very large Bunsen burner, while in the Fletcher furnace the flame is broken up into a number of smaller ones. In using these furnaces, it is well to remember a number of facts: (1) The furnace should always be heated and cooled slowly, so as to secure a long service from it. (2) There are a number of ways to regulate the heating, as by controlling the air admitted to the gas in the mixer; by the damper in the pipe; by the damper which closes the hole in the top. Familiarity with the effect produced by the management of each of these variables is highly desirable. (3) The crucibles employed in the furnace are heavy, and the furnace linings are more or less fragile. Care must be exercised in placing the crucible in the furnace and in removing it. (4) The student should hold himself responsible for attention to the furnace during operation, as well as for turning out the gas at the close of the experiment. (5) Reactions in a furnace are usually confined to a sintering together of unfused materials or take place in very viscous liquids. In either case, mixing during the reaction is very slow, and the charge should be very intimately mixed before heating to secure favorable results. (6) Fused materials are, in general, very corrosive, so that judgment must be used in selecting crucibles made of materials adapted to the reaction.

The following exercise is chosen to give a little experience with a furnace.

EXERCISE 21. CHROMIC OXIDE, Cr_2O_3

Pulverize 75 g. of commercial potassium dichromate in a mortar and mix it with an equal weight of ammonium chloride, rubbing the two ingredients intimately together. Place the mixture in a Hessian crucible and gradually heat in the gas furnace to a strong glow until no more vapors are given off. After cooling the crucible, scrape out the green oxide as well as possible, grind it up in a mortar if necessary, and boil it in about a liter of water. Decant the water and repeat with a new supply as long as the water turns yellow. Finally, pump the oxide upon a filter and dry on the hot plate.

The ammonium chloride acts as a reducing agent, reducing the chromic anhydride of the dichromate to the green sesquioxide. The reaction is not a simple one but consists of a number of independent reactions.

References: Friend, VII (III), 33; Mellor, XI, 176; Frankforter, *J. Am. Chem. Soc.*, **32**, 178 (1910).

Additional Exercises: Ultramarine, Thorpe, Dictionary; Wienard's blue, Jordan, *Z. angew. Chem.*, **6**, 684 (1893); reduction of $BaSO_4$ to BaS; burning pure marble to CaO.

VIII. ELECTROLYTIC PROCESSES

In a number of instances, it has been found not only possible but profitable to utilize electrical energy in the preparation of chemical materials, both in the laboratory and in the industries. For success in such work, careful attention must be paid to many details such as accurate control of intensity of current, current density at the electrodes, and the concentration of the electrolyte; and there must be available a suitable source of current (three or four storage cells), ammeter, voltmeter, and a variable resistance—best, a slide rheostat. It is usually possible to construct the working cells from ordinary laboratory supplies. For full details of all such apparatus, the student must refer to some good book on this special subject.

In all electrolytic processes, there are so many variable factors that close attention to all details is necessary as well as reasonable inventiveness on the part of the student. Careless or wholly mechanical work is almost sure to end in failure.

In general, in an electrolytic process, oxygen is evolved at the anode, and hydrogen at the cathode. If these electrodes are in different compartments, with a suitable electrolyte we may expect to have reactions of oxidation taking place in the anode compartment and reactions of reduction in the cathode compartment. In inorganic chemistry, the more successful electrolytic preparations are chiefly those of oxidation; while in organic chemistry, reactions of both oxidation and reduction are often successful. In inorganic chemistry, reactions of reduction are usually effected in simple ways. The several units of the necessary apparatus are connected as shown in Fig. 10.

References: Elbs, Electrolytic Preparations (1904); Mantell, Industrial Electrochemistry (1931); Perkins, Practical Methods of Electrochemistry (1905).

EXERCISE 22. BARIUM FERRATE, $BaFeO_4 \cdot H_2O$

Arrange an electrolytic cell by placing a porous battery jar of about 4 cm. diameter in a 350-cc. beaker and suspending in each compartment a cast-iron electrode. The walls of the jar should be as thin as possible, since the resistance increases rapidly with wall thickness. Hold the electrodes in place by burette clamps the rubber-covered jaws of which will serve as insulators. The electrode within the porous cell should be the cathode.

Prepare the electrolyte to be used in both cells by dissolving 50 g. NaOH in 150 cc. of water. Pour the electrolyte into the two compartments so that its level is about the same in each. Heat the beaker to 70° throughout the experiment, either by an electric heater or by a well-regulated gas flame.

Secure connections with two storage cells (more if necessary), placing a variable resistance and an ammeter in series with the cell and a voltmeter across the terminals of the electrodes (Fig. 10). No considerable action occurs until the voltage across the electrode terminals is raised to about 2 volts, and through the experiment it should be about 2.5 volts. The most favorable current density is given as 0.001 amp. per square centimeter; but in a cell of this type, it is likely to be two or three times that value.

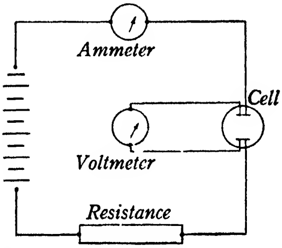


FIG. 10.—Apparatus for electrolytic preparations.

When the current is well adjusted, a dark-red color appears immediately around the anode, and the solution in the anode cell soon becomes dark red throughout. After about 2 hr., stop the action, remove the cathode cell, and dilute the anode solution with an equal volume of water. Filter on an asbestos mat, if necessary, and add a saturated solution of barium hydroxide or barium chloride as long as a red precipitate forms. Wash the precipitate several times by decantation with hot water, collect it on a filter, and wash it free of alkali. Dry at a temperature not to exceed 100°. The preparation is never very pure, and the yield is small. If at any time the electrodes become "passive," reverse the current frequently for a few minutes at a time.

References: Friend, IX (II), 130; Mellor, XIII (2), 930; Haber and Pick, *Z. Elektrochem.*, **7**, 215, 712, 724 (1900); Grube and Gmelin, *ibid.*, **26**, 459 (1920).

EXERCISE 23. LEAD CHROMATE, $PbCrO_4$

In a large (2 l.) beaker, suspend three lead electrode plates, cut from sheet lead, about 1.5 cm. apart. Connect the middle plate as anode and the two outer ones as cathodes. In the beaker place an electrolyte consisting of 10 g. of sodium nitrate and 3 g. of potassium chromate dissolved in 1 l. of water. Prepare a solution of 7.5 g. of chromic anhydride, CrO_3, in about 20 cc. of water and from a dropping funnel allow this solution to drop into the electrolyte at a rate of about half its volume in 2 amp.-hr. during the electrolysis to maintain the chromate concentration. In a specific experiment, the anode surface was 85 sq. cm. on each side of the anode; the most favorable current density was 0.0059 amp. per square centimeter, which for this cell made a current of 1 amp. with a voltage across the terminals of 2.3 volts.

As soon as the current is turned on, lead chromate begins to roll off the anode and fall to the bottom of the cell. Very little adheres to the anode plate. After about 2 hr., shut off the current and allow the suspended particles to settle. Decant the clear liquid, wash the precipitate with hot water by a second decantation, collect the solid on a filter, and dry it in the air oven. The yield should be very nearly quantitative for the current used.

Reference: Le Blanc and Bindschedler, *Z. Elektrochem.*, **8**, 255 (1902); Isenberg, *ibid.*, **9**, 275, 547 (1903).

Additional Exercises: $KMnO_4$, Henke and Brown, *J. Phys. Chem.*, **24**, 608 (1920); Wilson and Horsch, *Trans. Am. Electrochem. Soc.*, **35**, 371 (1919); Lorenz, *Z. anorg. Chem.*, **12**, 393 (1896); Reduction of ammonium iron alum to Mohr's salt, Howe and O'Neal, *J. Am. Chem. Soc.*, **20**, 759 (1898).

PART II

PREPARATIONS ILLUSTRATING TYPES OF COMPOUNDS

Introduction.—Up to this point, the exercises have been chosen to illustrate the most effective way of overcoming difficulties that are likely to arise in the preparation of any given compound. Attention has been centered upon manipulative skill rather than upon the nature of the compound chosen or upon the character of the reactions and the types of the compounds.

The student will now profit by exercises chosen to illustrate the most familiar types of compounds and the reactions available to prepare them. In every exercise, the student should keep in mind the type being illustrated and should, through collateral reading, be forming a judgment as to how far the reaction may be considered to be a general one and to what limitations it is subject. New points in manipulation will frequently develop, and these should be noted, and the extent of their application should be kept in view.

It is obvious that the types selected for illustration must be a matter of choice and that the list could be extended indefinitely. Considerations of familiarity, of importance of the type, of instruction to be derived from the exercises, and the practical value of the specific compounds described have all contributed to the selection.

I. BINARY COMPOUNDS

A binary compound is one that is composed of but two elements, though these need not be in simple atomic ratio.

In the group, the most familiar members are the oxides, halides, hydrides (including the hydrocarbons), nitrides, sulfides, and carbides. Many methods are available for the preparation of binary compounds, and the most general ones will be illustrated by exercises.

1. The Union of Two Elementary Substances.—The most obvious way in which to prepare a binary compound is by the union of the two constituent elements, though in many cases this is not the most practicable way. Sometimes, the elements are first prepared in pure form and are then combined; in other cases, the preparation of the elements and their union is effected in one operation, as in the manufacture of calcium carbide and carborundum. In general, the more dissimilar the two elements the more likely they are to combine readily, but elements of the same general kind sometimes combine with ease, as is the case with chlorine and iodine, sulfur and phosphorus, or sodium and lead.

EXERCISE 24. MERCURIC SULFIDE, HgS (VERMILION)

The union of mercury and sulfur is effected in the most simple way of all by merely rubbing the two substances together. The product is a black, amorphous compound, quite unlike the bright scarlet crystalline mineral cinnabar. To convert it into the crystalline form, advantage is taken of the following principle: An amorphous form is more unstable than a crystalline form and tends to go over into it. The unstable amorphous form is also more soluble in solvents than the stable crystalline form. If, therefore, a solvent can be found in which both are slightly soluble, the amorphous form dissolves to saturation, but this produces a solution oversaturated with respect to the stable form, and some of this crystallizes out. More of the unstable form then dissolves, and the cycle continues until all of the product is in the crystalline state.

Place 50 g. of mercury and 20 g. of powdered sulfur in a mortar. Grind them together, adding a few cubic centimeters of ammonium sulfide from time to time and continuing the operation until all drops of mercury have disappeared and a black paste has been obtained. A suitable solvent for promoting the transformation of the black form into the scarlet is prepared by dissolving 12 g. of solid potassium hydroxide in 60 cc. of water. Scrape the black paste into a 200-cc. Erlenmeyer flask, using the solution to wash it in and being careful not to add more water. The transition is best effected at from 45 to 50°, but the temperature must not rise above the latter point. By a few trials with a small flask containing water and provided with a thermometer, a place may be found either in an air oven or on blocks of wood placed on the hot plate where this temperature is moderately constant. If the temperature goes much above the right point, the color will not be good. Shake up the contents of the flask from time to time and keep it stoppered with a cork provided with a long glass tube to act as a condenser and prevent rapid evaporation. Continue the heating for several days until a bright scarlet product is obtained.

When the transition is complete, wash the product several times by decantation to remove as much of the excess sulfur as possible. Then stir up the scarlet product and quickly pour it off from the heavier mercury, repeating the process until only mercury remains. Collect the vermilion suspended in water (the volume should be about 250 cc.) in an evaporating dish and add about 10 g. of sodium sulfite. Boil the mixture for some time until the remaining sulfur has been dissolved by the sulfite. Finally, remove any very fine powder by decantation, filter the bright scarlet product on a Witte plate, and dry it on the hot plate.

The sulfides of the elements in general may be made by heating the elements with sulfur, but it is not usually possible to find a solvent from which they can be crystallized in this way.

References: Mellor, IV, 944; Friend, III (II), 274; Kastle and Clark, *Am. Chem. J.*, **22,** 473 (1899); Allen and Crenshaw, *Am. J. Sci.*, (4) **34,** 367 (1912); Knox, *Z. Elektrochem.*, **12,** 477 (1906).

Topic: Transition points, Findlay, The Phase Rule, pp. 32, 227, 279, 6th ed. (1927); Ephraim, pp. 195, 464.

Additional Exercises: Copper oxide from copper (for combustion); bismuth iodide.

EXERCISE 25. MAGNESIUM NITRIDE, Mg_3N_2

In general, the nitrides of most of the metals and many of the nonmetals may be prepared by heating the elements together. Owing to the inactivity of nitrogen at ordinary temperatures, it is usually necessary to heat to a very high temperature. Consequently, the formation of nitrides is often observed in electric furnace work. Magnesium nitride is one of the nitrides easiest to prepare.

Fill a small iron crucible about one-half to two-thirds full of magnesium powder. Bore a pinhole in the iron lid and then place the lid on the crucible. Lute the lid to the crucible with wet asbestos pulp and close the hole with the same material. (If a lid is not available, twist the crucible on a piece of asbestos board like a biscuit cutter until a deep groove has been cut in it and then lute it to the crucible as before.) Dry the crucible and its contents in an air oven or on the hot plate and when they are dry pierce a small hole in the asbestos plug with a pin. Place the crucible in a circular hole in a piece of asbestos board, so that most of the crucible is below the board (Fig. 11), and support the board on a ring stand. Heat the crucible with a blast flame directed against its sides, taking care that as little as possible of the flame come near the lid. Also, rotate the crucible from time to time so that all sides may be heated. After about half an hour of heating, allow the crucible to cool and remove the lid. A layer of white oxide will be found on top of the product, and under this a yellowish mass of magnesium nitride. If the heating has been insufficient, this will be spotted through with unchanged magnesium. To prepare the pure nitride, magnesium must be burned in a current of pure nitrogen. The latter is now available commercially in compressed form.

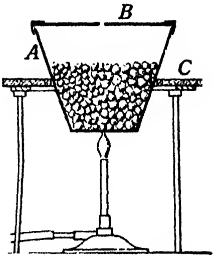


FIG. 11.

Like many [illegible] nitrides, magnesium nitride is at once hydrolyzed by contact with water, and even in moist air the odor of ammonia is very noticeable about the preparation. Some of the nitrides are, however, very stable toward water, notably some of the nitrides of phosphorus and titanium.

References: Friend, III (II), 70; Mellor, VIII, 104; Eidmann and Moeser, *Ber.*, **34**, 390 (1901); Friederich and Sittig, *Z. anorg. allgem. Chem.*, **143**, 293 (1925).

Additional Exercise: Aluminum nitride, AlN, White and Kirschbraun, *J. Am. Chem. Soc.*, **28**, 1343 (1906).

Halogen Compounds.—Practically all of the elements unite with chlorine, bromine, and iodine to form the corresponding halogen compounds. With the metals, well-defined solid salts are formed, save in cases in which the metal has a high valence and is a metallo-acid element. With the nonmetallic elements, the halogen compound is likely to be a low-melting solid or liquid with few of the characteristics of a salt; they are decomposed by water, undergoing extensive or complete hydrolysis. As a consequence, they fume strongly in moist air. The liquid representatives of the class usually have a high density and refractive index. The easily volatile haloids can be prepared by conducting a stream of the gaseous halogen element over the other element, and as a rule very little heating is required to bring about this action. The halogen compounds of carbon are exceptional in their chemical stability.

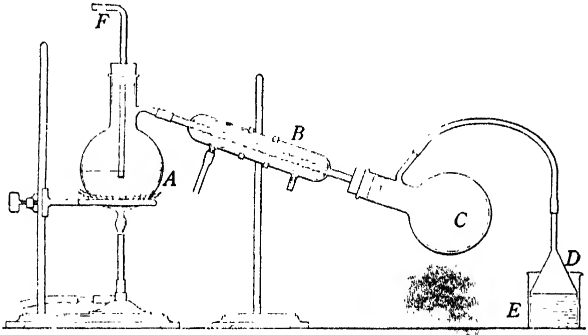


FIG. 12.—Preparation of volatile chlorides.

EXERCISE 26. SULFUR MONOCHLORIDE, S_2Cl_2; PHOSPHORUS TRICHLORIDE, PCl_3; STANNIC CHLORIDE, $SnCl_4$

The following directions will serve for the preparation of the chloride of sulfur (S_2Cl_2), phosphorus (PCl_3); or tin ($SnCl_4$). All of the apparatus used must be entirely dry. Place about 25 g. of sulfur, phosphorus, or mossy tin in a 200-cc. distilling flask *A* (Fig. 12), connected with a good condenser *B*. Fit another distilling flask *C* to the condenser to act as a receiver, making a tight connection with a cork. To absorb the excess of chlorine, connect a funnel *D* of about 8 cm. diameter by its stem to the exit tube of the second distilling flask and dip the rim of the funnel *just under* the surface of the concentrated solution of sodium hydroxide contained in a good-sized beaker *E*. This arrangement avoids back pressure and provides good absorption. It is better than a wash bottle. If phosphorus is used, the white modification should be cut into pieces small enough to slip down the neck of the flask easily. The cutting should be done under water in a roomy evaporating dish, each piece being picked up with tongs, dried with filter paper, and dropped into the flask *A*, the greatest care being exercised not to touch the phosphorus while it is out of the water. Provide a well-fitting stopper for the distilling flask, arranging a right-angled tube *F* to pass through the stopper and reach to just above the material in the flask. Pass *dry* chlorine into the flask through this tube, at the same time heating the sulfur to a point somewhat above its melting point but applying no heat to the phosphorus or tin. Keep the end of the tube *F* just above the surface of the material in the flask. Most of the sulfur monochloride will distill over into the receiver as it is formed, while the phosphorus chloride and the tin tetrachloride will to a large extent remain in the flask. When the reaction is complete, heat the flask and distill the liquid into the receiving flask *C*. Clean and dry the flask *A*, reverse the position of flasks *A* and *C*, and redistill, saving the portion which comes within 5° of the proper boiling point. The product should be poured into a dry bottle, and the stopper sealed with sealing wax.

The dry chlorine used in these preparations may be obtained in either of several ways: (1) It may be drawn directly from a tank of liquid chlorine. (2) Carefully place about 500 g. of rather coarse pyrolusite in a round-bottomed flask of about 1,500 cc. capacity and pour on it a liter of commercial (concentrated) hydrochloric acid. Provide the flask with a safety thistle tube, dipping into the liquid. Place the flask on a sand bath, taking care first to rotate the flask until all of the pyrolusite has become wet with the acid. Fill a gas-washing flask half full of sulfuric acid and pass the chlorine through the acid and then into the distilling flask containing the sulfur. Regulate the evolution of chlorine by a very small flame placed under the sand bath. (3) Instead of the pyrolusite, solid potassium permanganate (200 g.) may be placed in the flask, and the hydrochloric acid may be added drop by drop from a dropping funnel used instead of the thistle tube. This costs a little more but is under much better control.

References: (S_2Cl_2) Friend, VII (II), 76; Mellor, X, 633; Mann, Pope, and Vernon, *J. Chem. Soc.*, **119,** 636 (1921). (PCl_3) Mellor, VIII, 999; ($SnCl_4$) Friend, V, 346; Mellor, VII, 436; Lorenz, *Z. anorg. Chem.*, **10,** 44 (1895).

Additional Exercises: Phosphorus bromide, PBr_3; antimony chloride, $SbCl_3$.

2. Double Decomposition.—Many binary compounds may be regarded as salts of definite binary acids as well as compounds formed by the union of two elements. Among such compounds are the metallic halides, sulfides, selenides, tellurides, and peroxides. Many salts of these acids may be made by neutralizing a soluble base with the appropriate acid; a much larger number may be made by the method of double decomposition (Exercise 15).

EXERCISE 27. STANNOUS SULFIDE, SnS

The method is based upon the precipitation of a solution of a stannous salt by hydrogen sulfide. The most available stannous salt is the chloride, which may be prepared as follows: Place 12 g. of mossy tin in a 15-cm. evaporating dish and add 50 cc. concentrated hydrochloric acid, warming gently if necessary and replacing the acid if it evaporates before the tin has passed into solution. The solution of the tin is very slow and may be hastened by keeping it in contact with a small piece of platinum foil (phenomenon of overvoltage). Finally, evaporate almost to dryness and dissolve in about 1,000 cc. of water contained in an Erlenmeyer flask provided with a one-hole stopper and a delivery tube reaching almost to the bottom of the flask. Conduct hydrogen sulfide into the hot solution through the delivery tube until all of the tin has been precipitated as a brownish-black precipitate. It should be remembered that during precipitation the acidity of the solution is constantly increasing and that a condition of equilibrium is likely to be reached before the precipitation is complete. This condition can be prevented by adding ammonia from time to time during precipitation, taking care that the solution always remains acid, or by adding about 25 g. of sodium acetate at the outset. It should also be remembered that a large volume of H_2S will be required to precipitate so much tin.

When the precipitation is complete, allow the precipitate to settle, decant off as much as possible of the clear solution, and finally collect the stannous sulfide on a fluted filter paper (not too large), washing it several times with very dilute hydrochloric acid and drying it on the hot plate. The yield should be 15 g. The hydrogen sulfide may be drawn from the large generator used in the laboratory for qualitative analysis, or it may be generated in a Kipp apparatus charged with lumps of ferrous sulfide and hydrochloric acid. Make a rough calculation of the volume of H_2S required

References: Mellor, VII, 465; Friend, V, 356.

Additional Exercise: Barium peroxide from hydrogen peroxide.

Topic: Overvoltage, Bennett and Thompson, *J. Phys. Chem.*, **20,** 296 (1916); Möller, *Z. phys. Chem.*, **65,** 226 (1909); Newbery, *J. Chem. Soc.*, **109,** 1359 (1916); Newbery, *J. Am. Chem. Soc.*, **41,** 1887–1898 (1919).

EXERCISE 28. CRYSTALLINE STANNIC SULFIDE, SnS_2

Stannic sulfide may be prepared as a yellow amorphous precipitate by double decomposition of a stannic salt with hydrogen sulfide. The crystalline modification, known as mosaic gold, may be prepared by sulfurizing stannous sulfide in the following way:

Mix together intimately 15 g. of stannous sulfide, 5 g. of sulfur, and 5 g. ammonium chloride or other quantities in this ratio. Place the mixture in a hard glass test tube the dimensions of which are about 2 by 15 cm. Clamp this loosely in a burette clamp in a nearly horizontal position, the clamp being attached to a ring stand at a height to allow of convenient heating of the tube. Heat the tube slowly through its length with a smoky flame, holding the burner in the hand and rotating the tube in the clamp by twirling the rim between the fingers so as to heat the tube on all sides. Have at hand a stirring rod to push back the material into the tube in case the evolution of gas should tend to force it out. Regulate the temperature so as to maintain a steady and slow evolution of fumes of ammonium chloride. Finally, beginning at the bottom of the tube, heat somewhat more strongly with the nonluminous flame, driving all ammonium chloride and excess of sulfur from the tube but not going beyond a very low red heat. If this final heating is neglected, there will be some impurities in the product; but high temperature should be avoided, since this will decompose the stannic sulfide. The product should be a mass of orange-yellow flaky crystals which, when rubbed between the fingers, leave a shining film like graphite.

The ammonium chloride does not figure in the equation for the reaction, but its volatilization serves to absorb excess of heat and prevents overheating of the sulfide. The latter decomposes at a temperature not much above that at which it is formed when no ammonium chloride is present. It may be that the latter lowers the temperature at which stannous chloride combines with sulfur, and it may have some other effect in producing good crystals. Its chief function, however, seems to be that of a heat absorber. Apparently, better results are obtained with precipitated stannous sulfide than with the purchased material.

References: Mellor, VII, 469; Friend, V, 357; Lagutt, *Z. angew. Chem.*, **10**, 557 (1897).

3. The Preparation of a Chloride by the Action of Sulfur or Carbon Chloride upon an Oxide.—An interesting reaction, which is not a double decomposition in the usual sense, takes place when a volatile chloride of a nonmetallic element is conducted over a hot oxide or a salt of any oxygen acid. An example of such reaction is shown in the equation

$$2Cr_2O_3 + 6S_2Cl_2 \rightarrow 4CrCl_3 + 3SO_2 + 9S.$$

A great many oxides, sulfates, silicates, and similar oxygen compounds may be decomposed in this way and converted into chlorides. Instead of sulfur chloride, it is often of advantage to use carbon tetrachloride, CCl_4, or phosgene, $COCl_2$.

In a similar way, sulfides may be made by the action of carbon disulfide on an oxide.

References: Mellor, X, 643; Friend, VII (III), 25; for CCl_4, Demarcay, *Compt. rend.*, **104,** 111 (1887); for S_2Cl_2, Matignon, *ibid.*, **138,** 631, 760 (1904); for $COCl_2$ Chauvenet, *ibid.*, **152,** 87 (1911); for decomposition of minerals by S_2Cl_2, Lukens, *J. Am. Chem. Soc.* **35,** 1464 (1913).

EXERCISE 29. ANHYDROUS CHROMIC CHLORIDE, $CrCl_3$

Provide a small combustion furnace of at least 10 burners and a piece of combustion tubing of rather large bore long enough to project about 3 in. at each end of the furnace. Place 10 to 15 g. of chromic oxide (Exercise 21) in a thin layer on the bottom of the combustion tube or in a porcelain boat. With a rubber stopper, attach a small distilling flask to one end of the tube, placing in the flask about 50 cc. of sulfur chloride (or carbon tetrachloride). To the other end of the tube connect a funnel dipping into a beaker containing a concentrated solution of sodium hydroxide. Incline the furnace so that any liquid tending to condense in the delivery tube of the distilling flask will drain back into the flask. Heat the central part of the tube to a bright red heat and then very carefully heat the distilling flask until the sulfur chloride is just boiling. In this way, a steady stream of the vapor of sulfur chloride is passed over the chromic oxide. Continue the heating until almost all the liquid has boiled away. Then detach the absorption funnel and slowly cool the combustion tube, turning the burners down and out very slowly. When the tube is cool, remove it from the furnace. Scrape out the violet chromic chloride as well as possible and collect in a bottle.

The product is practically insoluble in water and in boiling, dilute hydrochloric acid; but if even a very little chromous salt is added, it dissolves rapidly, forming a green solution. The chromous salt may be secured by dissolving a bit of metallic chromium in hydrochloric acid (see Ephraim, pages 237 and 251).

When volatile chlorides are prepared in this way, as for example, titanium chloride from rutile, the product must be passed through a good condenser and collected in a receiver protected from the air. It will then be mixed with some unchanged sulfur chloride and will have to be fractionally distilled.

Additional Examples: $AlCl_3$ from Al_2O_3; $FeCl_3$ from Fe_2O_3; TiS_2 from TiO_2 and CS_2, Rose, *Pogg. Ann.*, **15**, 145 (1829).

4. The Preparation of a Hydride.—Strictly speaking, a hydride is the binary combination of hydrogen with a more positive element (metal); but for convenience we shall use the term to denote any binary compound of hydrogen. In addition to a number of methods applicable in special cases, there are two general methods available in the preparation of hydrides. The most general one is the direct union of hydrogen with another element, thus:

$$2Na + H_2 \rightarrow 2NaH,$$
$$Cl_2 + H_2 \rightarrow 2HCl.$$

The second method, applicable to the preparation of the hydrides of many of the nonmetals, depends upon the hydrolysis of an appropriately chosen binary compound:

$$PBr_3 + 3H_2O \rightarrow P(OH)_3 + 3HBr,$$
$$Al_2S_3 + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2S,$$
$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2,$$
$$Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3.$$

In general, that element of the binary compound having the greater affinity for oxygen will take the hydroxyl group from water; the element having the less oxygen affinity, the hydrogen. If the hydride is soluble in water and is a moderately strong acid, a state of equilibrium will result:

$$NaCl + H_2O \rightleftarrows NaOH + HCl,$$
$$CaS + H_2O \rightleftarrows Ca(OH)_2 + H_2S.$$

In this case, a strong, nonvolatile acid (H_2SO_4) must be added to neutralize the base and bring the equilibrium to a conclusion.

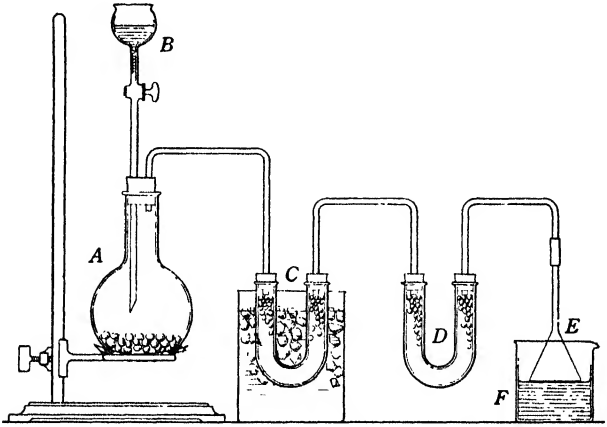


FIG. 13.—Preparation of hydrogen bromide.

References: Stock, Hydrides of Boron and Silicon (1933); Paneth, Radio Elements as Indicators and Other Selected Topics in Inorganic Chemistry (1928); Stewart, Recent Advances in Physical and Inorganic Chemistry, 6th ed. Chap. XVI (1930).

EXERCISE 30. HYDROGEN BROMIDE, HYDROBROMIC ACID, HBr

Obtain a 500-cc. round-bottomed flask *A* (Fig. 13), a two-holed stopper to fit, a drop funnel *B* (100 cc.) provided with a beveled delivery end, two U tubes *C* and *D* about 15 cm. in height, and a funnel *E* (5 cm.). By means of right-angled glass tubes, connect the flask with the two U tubes in series, and the last tube with the stem of the funnel.

Place about 30 g. of sand on the bottom of the flask to protect the glass from the heat of the reaction. On this place a mixture of 50 g. of sand and 20 g. of red phosphorus, the sand being intended to dilute the phosphorus. Moisten the whole (without shaking) with 40 cc. of water, insert the dropping funnel *B* in the second hole of the stopper, and mount the flask on wire gauze on a ring stand, with a retort clamp. Fill the U tube *C* with bits of broken glass or beads to act as a condenser for bromine vapors, immersing the tube in a beaker of ice water. Fill the second tube with glass beads which have been rubbed in red phosphorus, moistening with just enough water to make it a little sticky. Arrange a beaker with about 100 cc. of water just below the inverted funnel and at a height so that the rim of the funnel just dips into the water. It is well to have a good-sized evaporating dish filled with cold water at hand so that if the reaction in the flask becomes too rapid, the flask may be dipped in the water to cool it.

Place about 50 cc. of bromine in the dropping funnel *B*, exercising the greatest care in handling the liquid not to inhale the fumes or spill it on the fingers. Very cautiously allow the bromine to drop upon the phosphorus. At first, the falling of each drop will be accompanied by a flash of flame, and the drops must fall so slowly that the red fumes are not swept over into the U tube in any considerable quantity. Later, the rate of dropping may be increased. The gaseous HBr formed by the hydrolysis of PBr_3 will be absorbed in the beaker of water, and no bromine should come over. If some should come over, add a small quantity of red phosphorus to the liquid, and set it aside in a stoppered bottle for a day or so until the liquid becomes nearly colorless.

In either case, the liquid should now be distilled slowly from a distilling flask, and the distillate caught in a test tube. From time to time, the distillate should be tested with a few drops of silver nitrate until a strong test for hydrobromic acid is obtained. The receiver should then be changed, and all that comes over collected. It will be found that the distillation proceeds at constant boiling point.

On long standing, the solution of hydrobromic acid will turn brown owing to the liberation of bromine. Hydrobromic acid is much less stable than hydrochloric acid and, as a chemical reagent, acts as a moderately strong reducing agent. An interesting compound, cupric bromide, may be made by neutralizing a portion of the hydrobromic acid with copper oxide or carbonate and evaporating to dryness on a hot plate. At first, the solution is green, but it turns to a deep purple brown as it becomes concentrated and finally deposits very soluble crystals which resemble iodine in a superficial way.

Hydriodic acid may be made in an entirely analogous way, but the fact that iodine is a solid modifies the procedure slightly. The iodine and red phosphorus are roughly mixed together, preferably with a little sand, and placed in the flask. The water is added drop by drop through the dropping funnel. Otherwise, the procedure is entirely analogous.

For some special methods for hydrides, see Exercise 44 (barium hypophosphite). Also, look up the preparation of NH_3 and $NH_2{\cdot}NH_2$.

References: Friend, VIII, 158; Mellor, II, 167; Linnemann, *Ann.*, **161,** 198 (1872); Organic Syntheses, Vol. I, p. 2 (1921).

Topic: Constant-boiling mixtures; consult textbooks on physical chemistry.

5. Reduction of Ternary Compounds.—Another general method for preparing binary compounds is the reduction of various oxygen salts and acids (ternary compounds). The reduction of an acid is usually accompanied by dehydration, so that oxides of the acid-forming element are obtained. Thus, mild reduction of nitric acid yields the dioxide NO_2 or nitric oxide, NO, (Exercise 18); sulfuric acid yields SO_2 (Exercise 19); and arsenic acid, H_3AsO_4, yields As_2O_3. No further exercises will be given on reduction of acids.

The reduction of an oxygen salt usually takes place with much more difficulty. The salt is a solid and must, as a rule, be heated sharply with a reducing agent to undergo reduction. Sulfates, phosphates, and arsenates yield the corresponding sulfides, phosphides, and arsenides; and the same principle holds with many other salts. With an electric furnace, using carbon as a reducing agent, these reductions are easily effected, and many of them can be effected in the white heat of a coke furnace. Not many are effected in a gas furnace of the usual type, but the sulfates of calcium, strontium, and barium can be reduced in this way.

EXERCISE 31. STRONTIUM SULFIDE, SrS

Finely powder 50 g. of celestite (or commercial strontium sulfate) and mix it with 20 g. of powdered charcoal. Pack the mixture into an earthenware crucible of as thin walls as possible and heat at the highest temperature of the furnace for about 2 hr. Allow the crucible to cool and test a small portion with dilute hydrochloric or nitric acid. If the residue is chiefly carbon, the reduction is successful; if a large amount of insoluble white material remains, the entire mixture should be ground with additional carbon and reheated. It is not practicable to purify the sulfide, though a partially purified product may be obtained by repeatedly shaking the mixture with chloroform and decanting while the carbon is still suspended, leaving the heavier sulfide behind each time. It is better at once to dissolve in acid, filter off the carbon, and evaporate to crystallization. Use hydrochloric, nitric, or acetic acid.

References: Friend, III (I), 172; Mellor, III, 740; Mourlot, *Ann. chim. phys.*, (7) **17**, 522 (1899).

Additional Exercises: BaS from $BaSO_4$; Ca_3P_2 from $Ca_3(PO_4)_2$.

II. INTERMETALLIC COMPOUNDS; SALTS OF HOMOATOMIC ANIONS

Compounds of two negative elements, such as SO_2, PCl_5, S_2Cl_2, As_2S_3, are very familiar. Compounds consisting of two metals are much less familiar, yet there are a great many of them. They are insoluble in all ordinary solvents and cannot be purified easily. They are made by melting the two metals together in the right proportion.

When two (or more) metals are melted together and the melt is allowed to solidify, the product is called an *alloy*. (Sometimes alloys contain nonmetals such as carbon.) Since metals are more widely used as alloys than in pure condition, the nature of alloys has been the subject of much study. It has been found that some metals are miscible in all proportions, while with other pairs there is a definite limit to solubility. When a melted mixture cools, there may crystallize out (1) pure metal, (2) a solid solution, (3) a definite compound, (4) or a mixture of any of these. In the simplest case, one or the other pure metal (components) crystallizes as the temperature falls until the lowest melting point of the mixture is reached (the eutectic point), and after that the two metals crystallize together in a fixed ratio but not as a compound. In Fig. 14, *A* is the melting point of the one metal, *B* that of the other, while *C* represents the lowest melting point of the mixture and also the percentage ratio of the eutectic mixture.

In other cases, a freezing-point curve represented in Fig. 15 is obtained. In this curve, the point *C* is a maximum freezing point between *D* and *E* and indicates that a compound has been formed between *A* and *B*, whose melting point is *t* and whose composition is shown at *AB*. The points *D* and *E* are eutectics, respectively, of *A* and *AB* and of *AB* and *B*.

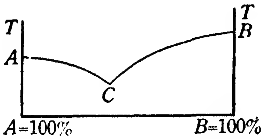


FIG. 14.

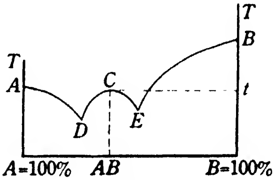


FIG. 15.

Some pairs of metals form several different compounds, and frequently these do not conform to our usual ideas of valence. For example, with tin and sodium there are known: Na_4Sn, Na_2Sn, Na_4Sn_3, $NaSn$, and $NaSn_2$. When the existence of any such compound is indicated by the freezing curve, it may be made by melting together the constituent metals in the proper proportion.

Kraus has shown that many of these compounds of the alkali metals with the less electropositive metals (some of which are soluble in liquid ammonia) possess many of the properties of typical salts. He calls these salts of *homoatomic anions.* It should be noted that in handbooks or indexes, these compounds are to be found under the caption "System"; thus; System Na-Sn; Na-Pb.

References: Desch, Intermetallic Compounds (1914); Schenk, The Physical Chemistry of the Metals (1919); Kraus, *J. Am. Chem. Soc.*, **44,** 1216 (1922); Johnson and Fernelius, *J. Chem. Educ.*, **7,** 981 (1930); Fernelius and Robey, *ibid.*, **12,** 64 (1935).

EXERCISE 32. SODIUM POLYPLUMBIDE, Na_4Pb_9; SODIUM POLYSTANNIDE, $NaSn_2$

For preparing any intermetallic compound of low-melting metals, especially if one metal is an alkali metal, proceed as follows: Obtain a piece of iron pipe about 1.5 by 12 in., with a solid plug welded into one end and fitted with a screw cap at the other. Thoroughly clean the inside of the pipe (bomb) with sandpaper or emery paper, wrapped around a round stick. Weigh 5 g. of sodium (8.5 g. of potassium) as free as possible from oxide and 100 g. of lead (51.5 g. of tin) and rapidly slip the metals into the bomb. Screw on the cap, clamp the bomb in a nearly vertical position, and heat the lower end with a Méker or Fisher burner to a temperature above that of the fusion point of the heavier metal (lead, 327°; tin, 232°). Allow a short time for completion of the reaction, rotate the bomb to a nearly horizontal position, and allow it to cool. Loosen the polyplumbide (polystannide) by tapping the bomb gently with a hammer. Unscrew the cap and quickly transfer the product to a bottle and stopper well. The polyplumbide is a good drying agent of basic character. If liquid ammonia is available, dissolve a little of the compound in it and note the color of the solution.

References: Na-Pb, Mathewson, *Z. anorg. Chem.*, **50,** 171 (1906); Na-Sn, *ibid.*, **46,** 94 (1905); *cf.* Zintl and Harder, *Z. phys. Chem.*, **154A,** 47, 94 (1931).

EXERCISE 33. MAGNETIC ALLOYS OF MANGANESE AND ANTIMONY

Many alloys possess properties that would hardly be predicted from the known properties of the constituent components. For example, some of these alloys are magnetic, though neither of the components is markedly so (Heussler alloys). An example is the manganese-antimony alloy (intermetallic compound).

In a hard-glass test tube, fuse together equimolecular weights of finely divided antimony and manganese (Exercise 85). A reaction takes place, and after cooling the powdered alloy is attracted to a magnet like iron filings.

References: Heussler, *Trans. Faraday Soc.*, **8**, 180 (1912); *Z. angew. Chem.*, **17**, 260 (1904); **25**, 2253, 2651 (1912); Williams, *Z. anorg. Chem.*, **55**, 1 (1907).

III. THE PREPARATION OF SALTS

Among the simple salts, three classes are recognized, *viz.*, normal, acid, and basic.

1. Normal Salts.—As a rule the method employed in the preparation of a normal salt is some modification of the general plan of double decomposition. This may take the form of (1) neutralization; (2) the action of one salt upon another; (3) the displacement of a volatile or insoluble acid by a nonvolatile or soluble one; (4) the action of an acid upon a metal. In the last case it is to be remembered that acids will liberate hydrogen only with those metals which are above hydrogen in the electrochemical series; that action upon those which are below hydrogen must be preceded by oxidation; that an acid will soon cease to act upon a metal if an insoluble salt is formed which protects the metal, or if an insoluble oxide is formed upon the metal. Most of these principles have already been illustrated.

2. Acid Salts.—There are two general ways of preparing acid salts: (1) the action of an acid upon a normal salt and (2) the partial neutralization of an acid. The following example will illustrate a convenient mode of procedure.

EXERCISE 34. POTASSIUM TETROXALATE, $KHC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$

In this salt, one hydrogen atom in two molecules of oxalic acid is replaced by potassium. In other words, the oxalic acid is neutralized to the extent of one-fourth of its total acid value. Dissolve 100 g. of commercial oxalic acid in 900 cc. of water and filtrate from mechanical impurities. Measure off 200 cc. (or a trifle less than one-fourth of the solution), heat this portion to boiling; and neutralize with potassium carbonate. Neutrality may be inferred by the use of strips of litmus paper or by carefully noting when additions of carbonate no longer occasion any effervescence. Meanwhile, heat the remaining solution to boiling and then unite the two solutions. If a precipitate should occur, it must be redissolved by heating or diluting with a little hot water. When a clear solution is obtained, cool the liquid rapidly under the running tap, so as to obtain small crystals. When thoroughly cold, filter on a bare Witte plate and recrystallize from hot water in the same way as before. Finally, pump as dry as possible on the Witte plate and finish the drying upon absorbent paper placed on glass.

When carefully prepared and dried, the salt has a perfectly definite composition. In acid strength, it may be regarded as a tribasic acid and is often used to standardize acid and alkali solutions by direct weighings as well as for preparing a standard reducing solution.

References: Mellor, I, 387; Friend, I, 191; II, 114, 174; Provostaye, *Ann. chim. phys.*, (3) **4,** 457 (1842).

Additional Exercises: $NaHCO_3$; $NaHSO_3$; $KHSO_4$; $Ca(H_2PO_4)_2$.

3. Basic Salts.—Under basic salts are included hydroxyl salts, such as $Sb(OH)_2Cl$, as well as their anhydrides, the oxysalts, such as SbOCl. They are usually prepared (1) by treatment of a normal salt with a base or (2) by the hydrolysis of a normal salt. In general, these salts exhibit many of the characteristics of the base from which they are derived, and, since most of the bases are insoluble and noncrystalline, many of the basic salts share these characteristics.

References: Mellor, I, 394, 1009; Friend, I, 199; *cf.* Feitknecht, *Helv. Chim. Acta,* **16,** 427 (1933).

EXERCISE 35. BASIC LEAD CHROMATE, $PbCrO_4 \cdot PbO$

Prepare about 30 g. of normal lead chromate, $PbCrO_4$ (Exercise 23), by the double decomposition of lead acetate and potassium dichromate and wash the precipitate until it is free from soluble lead salts. Suspend the yellow chromate in a dilute solution of sodium hydroxide (1:20) and boil until the color has changed to a bright brick red. This material is a basic chromate known as *chrome red,* having the composition represented by the formula $PbCrO_4 \cdot PbO$:

$$2PbCrO_4 + 2NaOH \rightarrow PbCrO_4 \cdot PbO + Na_2CrO_4 + H_2O.$$

The quantity of sodium hydroxide used should slightly exceed that required by the equation.

References: Friend, V, 439; Mellor, XI, 301; Cox, *J. Am. Chem. Soc.,* **28,** 1701 (1906); Free, *J. Phys. Chem.,* **13,** 114 (1909).

EXERCISE 36. BASIC LEAD NITRATE, $Pb(NO_3)_2 \cdot Pb(OH)_2$

Dissolve about 50 g. of lead nitrate in 500 cc. of hot water and divide the solution into two equal parts.

Heat one to boiling and add a solution of sodium hydroxide as long as lead hydroxide is precipitated, taking care not to redissolve any of the precipitate by excess of the reagent. Wash the solid several times by decantation. Dilute the other half of the solution to about 500 cc., heat to boiling in an evaporating dish, and add the pasty lead hydroxide to it. Boil until any solid remaining in suspension is distinctly crystalline and gradually add water until all of the solid has been brought into solution. Some permanent turbidity may remain, due to lead carbonate. Filter the solution through a folded filter and set aside to crystallize. The basic salt separates from the cooling solution in the form of fine needles. Pump the crystals on a Witte plate and completely dry them on paper. The salt is somewhat hard to dry, and it should not be needlessly exposed to the air, since it absorbs carbon dioxide rather readily.

References: Friend, V, 422; Mellor, VII, 867; Strömholm, *Z. anorg. Chem.*, **38,** 444 (1904).

Additional Exercises: $Pb(NO_2)_2 \cdot Pb(OH)_2$, Abegg, III (2) 707; $Pb(C_2H_3O_2)_2 \cdot 2PbO \cdot 4H_2O$, Jackson, *J. Am. Chem. Soc.*, **36,** 2346 (1914).

EXERCISE 37. ANTIMONY OXYCHLORIDE, SbOCl

This salt can be prepared in crystalline form by the action of alcohol upon antimony chloride at a temperature of about 160°. The first product of the action appears to be a salt of the formula $Sb(OC_2H_5)Cl_2$, but above 150° this decomposes according to the equation

$$Sb(OC_2H_5)Cl_2 \rightarrow SbOCl + C_2H_5Cl.$$

To secure the necessary temperature, the reacting mixture must be heated in a sealed tube, strong enough to resist the pressure of the contained vapors, which may amount to 10 or 12 atmospheres.

Dissolve 5 g. of antimony chloride in 10 g. of absolute alcohol and carefully pour the solution into a hard-glass tube, sealed at one end. To avoid moistening the sides of the tube with the solution, it is better to place the solution in a small test tube and slip it into the larger sealing tube. Carefully seal the tube by heating it a few inches below the open end with a blast lamp, constantly rotating it and very carefully drawing it out to a tube of small diameter at the heated region. Then continue the heating, allowing the tube to melt together without drawing it, so that the sealed end may be thick and of uniform walls. When the seal is finished, cool the sealed end very slowly to anneal it properly. When the tube is cold, place it in a bomb furnace and gradually raise the temperature to about 160°. Unless the tube has been well sealed, it will likely burst under the pressure developed. Continue the heating for about 2 hr. and then gradually cool the furnace, allowing the tube to become quite cold before removing it. When it is cold, cut off the sealed end and shake the contents until the crystals can be washed out. Wash them with absolute alcohol and dry them on paper. If three equivalents of alcohol are used, the composition of the crystals is $Sb_2O_5Cl_2$.

References: Mellor, IX, 504; Schaeffer, *Ber.*, **1**, 135 (1868).

EXERCISE 38. BERYLLIUM BASIC ACETATE, $Be_4O(C_2H_3O_2)_6$

If materials are available, it is most instructive to prepare this unique compound. While usually given the name and formula of a basic salt, none of its properties agrees with this classification. It melts sharply at 285° and boils undecomposed at 330°. It is undoubtedly a highly "coordinated" compound, with the extra oxygen atom as the center of coordination.

Dissolve about 10 g. of commercial beryllium hydroxide or carbonate in acetic acid and evaporate to dryness on the hot plate. Dissolve the dry residue in boiling glacial acetic acid and set aside for crystallization. The salt is deposited in small colorless octahedra. These should be drained on a Witte plate and dried on paper. The salt is decomposed by water.

References: Urban and Lacombe, *Compt. rend.*, **133**, 874 (1901); Lacombe, *ibid.*, **134**, 772 (1902); Parsons, *J. Am. Chem. Soc.*, **26**, 738 (1904); Morgan and Bragg, *Proc. Roy. Soc.*, **104**, 437 (1923).

Topic: Coordination valence, Sidgwick, The Electronic Theory of Valency, (1929).

Additional Exercises: Zinc basic acetate, $Zn_4O(C_2H_3O_2)_6$, Auger and Robin, *Compt. rend.*, **178**, 1546 (1924).

IV. PREPARATION OF HYDROGEN SALTS (ACIDS)

As a rule, the inorganic hydrogen salts are familiar only in the condition of more or less concentrated solutions. A number of them cannot be isolated in pure form, because they decompose so readily into water and the anhydride (H_2CO_3; HNO_2; H_2CrO_4). In other cases, the melting point lies below ordinary observation ($HNO_3 \cdot 3H_2O$) (m.p., $-18.5°$). Some hydrogen salts or their hydrates can be obtained as crystalline solids by proper care, though their concentrated solutions are so viscous as to render spontaneous crystallization unusual (H_2SO_4; H_3AsO_4; H_3PO_4). By sufficient cooling and proper seeding, good crystals of these latter compounds can be obtained. It will be recalled that the two general methods of preparing acids are (1) double decomposition of their salts with a less volatile acid and (2) oxidation in the presence of water of a nonmetallic element or one of its lower oxides.

EXERCISE 39. HYDROGEN ARSENATE, $2H_3AsO_4 \cdot H_2O$

Pour the residue of arsenic left in the preparation of nitrogen dioxide (Exercise 18) into an evaporating dish and heat, with addition of nitric acid, until red fumes cease to be evolved. Then evaporate to a syrup to drive off excess of nitric acid. By varying the concentration of the product, and by seeding with a crystal of hydrogen arsenate if necessary, the product may be brought to crystallization. As a rule, the crystals are very small, but occasionally very large ones form, especially on long standing in winter weather. The deliquescent crystals should be collected on a Witte plate and dried on porous plates in a desiccator.

References: Mellor, IX, 140; Menzies and Potter, *J. Am. Chem. Soc.*, **34**, 1452 (1912).

EXERCISE 40. HYDROGEN PHOSPHATE, $2H_3PO_4 \cdot H_2O$

The compounds may have either the formula H_3PO_4 (m.p., 40°) or $2H_3PO_4 \cdot H_2O$ (m.p., 30°). In a round-bottomed flask of suitable size, place 1 part of white phosphorus and 16 parts of nitric acid of sp. gr. 1.2 together with a few crystals of iodine as a catalyzer. Provide the flask with a reflux condenser, painting the cork with black asphalt paint to protect it from the action of the nitric acid. Heat until all of the phosphorus has dissolved; then distill off most of the liquid and pour the residue into an open dish. Evaporate with several additions of concentrated nitric acid to oxidize all lower acids of phosphorus and finally concentrate in a platinum dish until the temperature of the solution reaches 150°. On cooling, if necessary with a freezing mixture, the liquid can be brought to crystallization. The crystals should be dried over phosphorus pentoxide in a desiccator. The crystals are isomorphous with those of hydrogen arsenate, so that the latter may be used as seed to start crystallization.

References: Mellor, VIII, 952; Smith and Menzies, *J. Am. Chem. Soc.*, **31**, 1183 (1909).

EXERCISE 41. HYDROGEN IODATE, HIO_3

Provide a suitable water bath and a long-necked Kjeldahl flask and support the flask (under the hood) so that the bulb is immersed in water. Weigh out 10 to 15 g. of iodine and place it in the flask along with six to seven times its weight of *fuming* nitric acid (density, 1.5). Heat the water so that it steams freely but does not quite boil, occasionally shaking the flask gently. The iodine is rapidly oxidized to iodic acid which appears as a white, crystalline solid. Filter upon an asbestos mat on a Witte plate and pump off the mother liquor. Then dissolve in about 15 cc. of hot water, collecting the filtrate in a test tube placed in the filter flask. Pour this into a small beaker and add rather more than an equal volume of concentrated nitric acid (density, 1.4), dissolving any precipitate which forms by heating. Set aside overnight in a cool place to crystallize. Decant the mother liquor as well as possible, break up the crystal mass in the bottom of the beaker, and dry on a porous plate or by heating in a clean dish on the hot plate. The product should be clear white in color. Hydrogen iodate is extremely soluble in water but much less so in nitric acid. When crystallized from nitric acid, however, the product is contaminated with the latter substance.

References: Friend, VIII, 237; Mellor, II, 301; Baxter and Tilley, *J. Am. Chem. Soc.*, **31**, 201 (1909); **32**, 1591 (1910). Preparation from $Ba(ClO_3)_2$ and I_2, Lamb, Bray, and Geldard, *J. Am. Chem. Soc.*, **42**, 1636 (1920).

Alternate Method.—Have at hand 300 to 400 cc. of hydrogen peroxide solution (3 per cent). In a 750-cc. flask, place 10 g. of very finely powdered iodine, 10 cc. of concentrated nitric acid, and 50 cc. of hydrogen peroxide solution and loosely stopper the flask with a glass stopper or a small funnel to minimize loss of iodine. Heat the mixture on the water bath to about 70°. Shake the flask from time to time when the solution fails to show a deep color due to dissolved iodine. Observe when the reaction starts, as shown by the first decrease in color. Whenever the solution again becomes deeply colored, add more hydrogen peroxide. Continue the process until the iodine is all oxidized and then rapidly evaporate the solution to a small volume.

To remove the nitric acid and the organic matter introduced with the peroxide (added as a negative catalyst), evaporate the solution to dryness in a small porcelain dish. Heat the residue in an air oven for at least 2 hr., first at 140 to 150° and later at 170 to 180°. Extract the iodic acid with boiling water and filter off and reject the dark-colored residue. Evaporate the solution to dryness and partially dehydrate the solid by heating it in an air oven at 150 to 200°, avoiding overheating.

Dissolve nearly all of the partially dehydrated solid in the minimum amount of hot water, filter, cool the filtrate, and place the clear solution in a crystallizing dish in a desiccator over anhydrous calcium chloride. If necessary, seed with a crystal of iodic acid. When but a very little mother liquor remains, reject this and wash the crystals with a few drops of cold water, drying them on paper.

Reference: Bray and Caulkins, *J. Am. Chem. Soc.*, **53**, 44 (1931).

V. THE PREPARATION AND REACTIONS OF OXYGEN SALTS

Apart from the salts of halogen acids, the great majority of the salts with which the chemist has to deal are derived from oxygen acids. For convenience, these acids may be classified into two groups: (1) those derived from some strictly nonmetallic element such as the halogens, carbon, nitrogen, phosphorus, sulfur, arsenic, and silicon; and (2) the metallo-acids. The latter may be defined as those acids which are derived from an element which, in the free state, has the properties of a metal but in its chemical conduct plays the part of an acid-forming element in addition to forming metallic salts. Among these elements are manganese, chromium, iron, vanadium, uranium, antimony, lead, and the platinum elements. The two classes will be taken up separately.

1. Salts of Ordinary Oxygen Acids.—Among the ordinary oxygen salts are included the oxyhalogens; the nitrates and the nitrites; the carbonates; the phosphates, phosphites, and hypophosphites; the sulfates and sulfites; the borates; and the silicates. These may be divided into (*a*) oxidizing salts and (*b*) reducing salts.

a. Oxidizing Salts.—As a rule, the acid representing the highest state of oxidation of an element is the common acid, is easily prepared in pure state at least in solution, and forms stable salts which are easily secured. They may be obtained by purifying the natural salts, by neutralization of the free acid, or by double decomposition. In cases in which the highest oxidized salt is not the common one, it is usually obtained by energetic oxidation of some lower salt or acid. For example, the arsenic acid (Exercise 39) may be neutralized to obtain an arsenate, or an arsenite may be oxidized to form one.

Many such oxidations are accomplished by anode oxidation (see Exercises 22 and 49).

EXERCISE 42. POTASSIUM PERCHLORATE, $KClO_4$

Potassium perchlorate is prepared from potassium chlorate, the oxygen required for the oxidation being derived from the decomposition of some of the chlorate. This takes place in accordance with either of two distinct equations. Such reactions are called auto-oxidations.

$$2KClO_3 \rightarrow KClO_4 + KCl + O_2,$$
$$4KClO_3 \rightarrow 3KClO_4 + KCl.$$

Place 50 g. of potassium chlorate in a clean porcelain evaporating dish, supported on a ring stand, and heat with a good Bunsen burner. At first, the salt melts to a clear liquid, from which bubbles of oxygen presently arise. Regulate the heat so that the liquid appears to boil quietly and maintain this steady temperature for an hour or longer, until the liquid shows a strong tendency to solidify. Allow the dish to cool and dissolve the solid cake in about 300 cc. of boiling water. Set aside to crystallize. The perchlorate is deposited in fine crystals resembling common salt, which are very little soluble in cold water. If the heating has not been continued long enough, flat shining spangles of chlorate will also deposit. If these are few in number, they may be removed by recrystallization; otherwise, the salt must be reheated. In a similar way, sulfites split into sulfates and sulfides.

References: Friend, II, 167; Mellor, II, 395; Scobai, *Z. phys. Chem.*, **44**, 319 (1903); Lehner, Stone and Skinner, *J. Am. Chem. Soc.*, **44**, 143 (1922); Farmer and Firth, *J. Chem. Soc.*, **125**, 82 (1924).

b. Reducing Salts.—As a rule, the salts which represent a lower stage of oxidation, such as the nitrites, sulfites, and phosphites, do not occur in nature. They may be prepared in a number of ways, among which are the following: (1) the reduction of a higher salt; (2) neutralization of the lower acid; (3) action of a base on a nonmetal; (4) various special methods. Most of these salts tend to take up oxygen and pass to the higher stage of oxidation, this oxidation sometimes being accomplished by simple exposure to air. They are, therefore, more or less strong reducing agents in chemical conduct.

(1) *Reduction of a Higher Salt.*—The reduction of a sulfate to a sulfide (Exercise 31) is an example of this type of reaction. A second example in which the reduction is partial is found in the following.

EXERCISE 43. SODIUM NITRITE, $NaNO_2$

This salt is prepared from the nitrate by reduction with lead:

$$NaNO_3 + Pb \rightarrow NaNO_2 + PbO.$$

Support an hemispherical iron dish of 10 cm. diameter (or an iron crucible) on a ring stand and place in it about 75 g. of sodium nitrate. Heat the nitrate until it melts and just begins to evolve bubbles of oxygen. While maintaining a steady temperature, drop in pieces of granulated lead or chopped-up lead pipe, stirring well with an iron rod (old round file) after each addition. A little more than the equivalent of lead should be added, since some of it will be oxidized by the air. For this reason, a flat iron sand-bath dish is not suitable for the experiment. The reduction of the nitrate is rapid, and if much lead is added at a time, the mass may become incandescent.

When all of the lead has been added, increase the heat somewhat, stir for five or ten minutes, and then allow the dish to cool. Place it in an evaporating dish containing enough water to cover it well and gently boil the water until the contents of the iron dish have become disintegrated and removable from the dish. Filter from the litharge and extract once with hot water. From a small generator pass carbon dioxide into the hot solution as long as any lead carbonate is precipitated but no longer. Filter, evaporate to about 100 cc., and allow to cool. If clear, well-formed crystals separate, they are likely to be undecomposed nitrate. Withdraw a few from the solution, dry on filter paper, and test with nitric acid. If they are the desired nitrite, they will evolve dense red flames. The nitrate forms larger and more transparent crystals, and is not nearly so rapidly soluble as the nitrite. Consequently, nearly all of the nitrates can be removed before the nitrite is collected. The nitrite is extremely soluble, so that the mother liquors should be worked over nearly to dryness.

References: Mellor, VIII, 473; Friend, II, 132; Morgan, *J. Soc. Chem. Ind.*, **27**, 483 (1908).

(2) *Neutralization.*—The preparation of reducing salts by neutralization requires no special comment. The most familiar examples are the soluble sulfites and sulfides. Since these are salts of weak, dibasic acids, it is not satisfactory to rely upon indicators for neutrality. The usual procedure is to prepare a solution of the base and divide it into two equal parts. One of these is saturated with the acid, producing the acid salt, and the other portion is then added, with the formation of the normal salt (example, preparation of $(NH_4)_2S$ as a laboratory reagent).

(3) *Action of a Nonmetal on a Soluble Base.*—Most of the nonmetals act upon a solution of a soluble base,

forming the hydride of the nonmetal together with one of its reducing acids. Among the nonmetals which act in this way are chlorine, bromine and iodine, producing the halogen hydride and the hypoacids (or the -ic acids if the solution is hot); sulfur, which produces hydrogen sulfide and sulfurous acid (and thiosulfuric acid as a secondary reaction); and phosphorus, which produces phosphine and several different acids, notably hypophosphorus acid. Since the base is always present in excess, all of these acids are neutralized and are obtained as salts.

EXERCISE 44. BARIUM HYPOPHOSPHITE, $Ba(H_2PO_2)_2 \cdot H_2O$

In a round-bottomed flask of about 1 l. capacity, prepare a solution of 80 g. of barium hydroxide in 800 cc. of water. Support the flask (hood) in a water bath which can be heated nearly to boiling. Under cold water, cut into small pieces 20 g. of white phosphorus (two-fifths of a stick) and add this to the solution. Provide a two-holed stopper for the flask and through one hole insert a right-angled tube reaching to the bottom of the flask and connected with the laboratory gas supply. Through the other insert a delivery tube extending just through the stopper and provided with a safety bulb. The end of the delivery tube dips under water in a suitable vessel, and just above it clamp a lighted Bunsen burner to insure the combustion of the phosphine which will be formed. Turn on the gas until the air has been displaced from the flask and then allow it to run slowly during the experiment. Heat the water bath almost to boiling. Phosphine is disengaged and burns at the surface of the liquid above the end of the delivery tube while the phosphorus goes into solution in the course of some hours. The flask should be carefully shaken from time to time to bring fresh liquid into contact with the phosphorus. When phosphine ceases to come off, remove the flask from the water bath, and filter from the insoluble residue (phosphorus, phosphate, phosphite). Conduct carbon dioxide into the hot solution until the excess of barium hydroxide is precipitated; filter; and evaporate to small volume, the final evaporation being conducted in a beaker. If the solution is turbid at 300 cc., filter again. Continue the evaporation until signs of crystallization appear; then cool and drop in about half of the volume of alcohol. Pump the crystals on a funnel furnished with a bulb or a marble (page 6) and work over the mother liquor for a second crop. Finally, recrystallize the united product from a very little water.

The mother liquor may be used to test the reducing power of the compound. A little added to sulfuric acid in a test tube and then brought to a boil liberates reduction products of the acid. Silver nitrate solution is quickly reduced to silver.

References: Friend, III (1), 244; Mellor, VIII, 884; Wurtz, *Ann.*, **43**, 322 (1842); Berlandt and Bachmann, *Arch. Pharm.*, (2) **172**, 237 (1865).

(4) *Special Methods.*—Many special methods are employed to produce reducing salts, particularly cathode reduction. The following exercise illustrates one of these special methods, *viz.*, the action of a metal (zinc) on sulfur dioxide.

EXERCISE 45. ZINC HYPOSULFITE, ZnS_2O_4

Into a 500-cc. Erlenmeyer flask put enough granulated zinc to cover the bottom. Pour over this about 150 cc. of *absolute* alcohol and provide the flask with a two-hole stopper. Through one hole insert a delivery tube dipping under the alcohol and through the other an exit tube connected with a gas bottle containing sulfuric acid to prevent moisture from backing into the flask. Generate sulfur dioxide by the action of sulfuric acid on copper and conduct the gas into the alcohol in the flask, at the same time cooling the flask to increase the absorption of sulfur dioxide. After the alcohol is completely saturated, the flask should be corked and allowed to stand. In about half an hour, a white microcrystalline precipitate of zinc hyposulfite begins to separate. More sulfur dioxide is then led in, and the process continued until an appreciable quantity of the salt has formed. It is then filtered off as rapidly as possible and dried over sulfuric acid in a desiccator charged with coal gas to prevent oxidation.

The salt is a powerful reducing agent and has been employed to reduce indigo to a colorless base. It is difficult to preserve unchanged and should be sealed in a bottle after displacing the air with coal gas.

References: Mellor, X, 183; Friend, VII (II), 225; Nabl, *Monatsh.* **20,** 679 (1899); Pratt, *Chem. Met. Eng.*, **31,** 11 (1924); *Ind. Eng. Chem.*, **16,** 676 (1924).

2. Salts of Metallo-Acids.—A number of elements are, in their physical properties, undoubted metals; but in their chemical conduct they are capable of acting as acid-forming elements as well as metals. Among these are chromium, manganese, molybdenum, tungsten, vanadium, tantalum, columbium, uranium, tin, antimony, and iron. It will be remembered that in an acid anhydride an element usually exhibits a rather high valence—four or above—while a metal has a valence of three or less. Consequently, one condition favorable to developing the acid qualities of a metallo-acid element is energetic oxidation. A second condition is the presence of a base to combine with the free acid as it is formed. Alkaline oxidation of any of these elements may therefore be expected to lead to the salts of a metallo-acid; conversely, acid reduction will change the metallo-acid element into a typical metal, acting as cation of a simple salt.

EXERCISE 46. POTASSIUM PERMANGANATE, $KMnO_4$

In a mortar, intimately grind 80 g. of potassium hydroxide with 40 g. of potassium chlorate. Place the mixture in an iron crucible or hemispherical dish of about 10 cm. diameter and melt it with a triple burner or blast lamp. Remove the flame and quickly add, a little at a time and with constant stirring with an old file or iron wire, 75 g. of manganese dioxide. The precipitated oxide is best, but finely ground pyrolusite will serve. Resume heating the contents of the dish, with stirring, until it has become dry and then at a dull-red heat for about 10 min. Pulverize the cooled mass in a mortar and boil with 1.5 l. of water, at the same time conducting into the solution a steady stream of carbon dioxide to change the manganate into permanganate. Continue this treatment until a drop of the turbid liquid placed on filter paper shows a pure pink border around the brown stain of oxides of manganese. Allow the solution to settle and filter on a Büchner funnel with an asbestos mat, washing well with hot water. Rapidly evaporate the filtrate to half its volume, filter again through asbestos, and evaporate to crystallization. The crystals cannot be brought into contact with paper but may be collected by the use of a marble or glass bulb (page 6). Pump the crystals as dry as possible and complete the drying on the hot plate or in an oven. Work over the mother liquors for a second drop. The latter may contain potassium chloride and should be recrystallized from water.

References: Friend, VIII, 298; Mellor, XII, 303; Böttger, *J. prakt. Chem.*, **90,** 156 (1863); Schlessinger *et al.*, *J. Ind. Eng. Chem.*, **11,** 317 (1919).

EXERCISE 47. POTASSIUM HYDROGEN PYROANTIMONATE, $K_2H_2Sb_2O_7 \cdot 4H_2O$

Dissolve 10 g. of antimony oxide or 15 g. of antimony chloride in the least possible excess of hydrochloric acid. Prepare a concentrated solution of potassium hydroxide containing about one and a half times the quantity of the reagent necessary to convert the antimony into potassium antimonite, $KSbO_2$. Then, with constant stirring, slowly add the antimony chloride to the potassium hydroxide. A clear solution should be obtained, but a moderate precipitate will not interfere with the preparation. Save out about one-tenth of the solution. Heat the remainder of the solution to 70 to 80°, using a thermometer as a stirring rod, and slowly add a rather concentrated solution of potassium permanganate until the liquid over the precipitated hydroxide of manganese becomes green. Add some of the solution reserved for the purpose until the green color just disappears and titrate back and forth until all the antimony has been oxidized. Filter on an asbestos mat on a Witte plate and rapidly evaporate on the water bath almost to dryness. Wash the salt which is obtained repeatedly with cold water and dry in the air.

The salt is very slowly soluble in water, and its solution at once produces a precipitate with sodium salts. It is one of the very few reagents which give such a test for sodium.

References: Mellor, IX, 449; Fremy, *Ann. chim. phys.*, (3) **23,** 408 (1848); Reynoso, *J. prakt. Chem.*, **53,** 127 (1851); Schou, *Z. anorg. allgem. Chem.*, **133,** 404 (1924); Knorre and Olschewski, *Ber.*, **18,** 2353 (1885).

EXERCISE 48. SALTS OF FERRIC ACID, H_2FeO_4

An impure sample of potassium ferrate, K_2FeO_4, may be prepared as follows: Dissolve sufficient ferric chloride, $FeCl_3 \cdot 6H_2O$, to correspond to 40 g. $Fe(OH)_3$ in 2 l. of hot water and precipitate the hydroxide with potassium hydroxide. Wash the precipitate repeatedly with hot water by decantation until nearly all chlorides have been removed and evaporate the suspended hydroxide to a volume of about 65 cc., bringing it into a porcelain dish that will hold about 250 cc. Break up 25 g. of solid potassium hydroxide into small pieces and add it to the ferric hydroxide, warming the mixture to insure solution.

Cool the mixture and from a dropping funnel slowly add 9 cc. of bromine, adding a little solid potassium hydroxide to maintain saturation and being careful to prevent strong heating of the mixture. Finally, add 10 g. of potassium hydroxide and heat slowly and with constant stirring to 60°, maintaining this temperature for ½ hr. and then cooling the mixture. The ferric hydroxide is oxidized by the hypobromite to K_2FeO_4, which is insoluble in a saturated solution of potassium hydroxide and separates as a reddish-black powder, along with crystals of potassium bromide and bromate. A small sample should dissolve completely in water, giving a deep purple color.

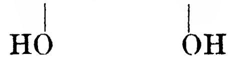
The solid may be filtered off on a filter of glass wool or asbestos, washed repeatedly with 96 per cent alcohol to remove KOH, dried, and preserved. It is not easy to purify this preparation from other potassium salts.

Barium ferrate, $BaFeO_4$, like barium sulfate and barium chromate, is insoluble and is the most stable of the ferrates. Dissolve the potassium salt in about ten times its weight of water, filter it through a filter paper previously moistened with the solution, and allow the filtrate to drop slowly into a constantly stirred excess of a solution of barium chloride. Filter off the deep-carmine red precipitate and dry it in a desiccator. When dry, the salt is stable; but when moist, it decomposes (see also Exercise 22).

References: Friend, IX (II), 131; Moeser, *J. prakt. Chem.*, (2) **56,** 425 (1897); Rosell, *J. Am. Chem. Soc.*, **17,** 760 (1895); Watts, Dictionary II, 547 (1919).

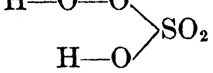
VI. PER-ACIDS AND THEIR SALTS

We distinguish a peroxide, such as BaO_2, from a dioxide of similar formula, such as MnO_2, by the fact that with acids the peroxide yields hydrogen peroxide (or ozonized oxygen), while the dioxide does not. There is a class of acids known collectively as *per-acids*, which likewise yield hydrogen peroxide (or ozonized oxygen) in acid solution; and from their conduct and modes of formation they may be regarded as sharing the peroxide structure —O—O— with hydrogen peroxide, H—O—O—H. In some cases, these acids may be represented as consisting of two acid radicals joined by the peroxide linkage —O—O—, thus: R—O—O—R. In other cases, they may be regarded as ordinary acids in which one or more hydroxyl groups have been replaced by the per-hydroxyl group —O—O—H. Three acids of sulfur illustrate these relationships:

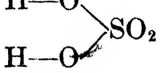


$$\begin{array}{c} O_2S—O—O—SO_2 \\ \;|\qquad\qquad\qquad\;| \\ HO\qquad\qquad\quad OH \end{array}$$

Di-per-sulfuric acid



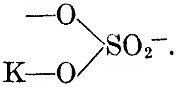
Mono-per-sulfuric acid; Caro's acid



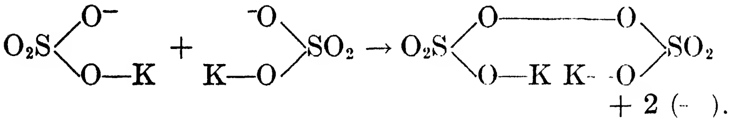
Sulfuric acid

These acids (or their salts) are usually prepared (1) by electrolytic (anodic) oxidation or (2) by the action of hydrogen peroxide on solutions of various acids or their salts.

1. Preparation by Anodic Oxidation.—When potassium hydrogen sulfate ionizes, we may consider the ions to be H^+ and



$\mathrm{\begin{matrix}-O\\ K{-}O\end{matrix}\!\!>\!SO_2^-}$. If we electrolyze such a solution, using an anode of small surface (high current density) such as a platinum wire, the anions converge to a limited area. On discharge, the anions combine in pairs, thus:



A similar result is obtained with some other polybasic acids, though not with all.

Reference: Price, Per-acids and Their Salts (1912).

EXPERIMENT 49. POTASSIUM PERSULFATE, $K_2S_2O_8$

Prepare an electrolytic cell as shown in Fig. 16. *T* is a large test tube about 3.5 cm. in diameter which is supported by a wire triangle in the beaker *B* containing ice water. A tube *S* about 1.5 cm. in diameter (made by cutting off the bottom of a tall test tube) is suspended in the tube *T* to prevent mixing of the electrolyte by gas bubbles from the electrodes. It can be held by a burrette clamp at the top. A platinum wire wound spirally outside *S* serves as cathode, and a stout piece of platinum wire inside *S* constitutes the anode. The surface of the anode must be measurable. This may be effected by sealing a stout piece of platinum wire in the end of a glass tube. If the projecting end is 1.6 cm. in length, and the wire is 0.1 cm. in diameter, the surface will be about 1 sq. cm. Connection is then made by a mercury contact within the tube. If heavy wire is not available, a platinum electrode with a heavy wire attached may be part of the laboratory equipment. All but a suitable portion at the end of the wire may be coated with some sort of laboratory wax or heavy shellac for insulation, and the wire inserted in the tube *S*. The internal resistance of the cell can be easily regulated by adjusting the height of the cathode and sliding the tube *S* up or down the clamp.

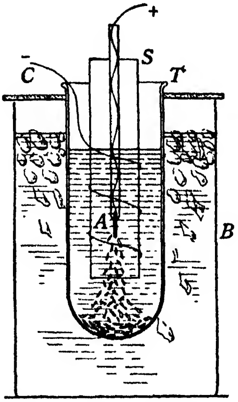


Fig. 16.—Preparation of potassium persulfate.

In the tube *T*, place a solution of potassium hydrogen sulfate saturated at about 0° or made by saturating a solution of sulfuric acid of density 1.3 with normal potassium sulfate, K_2SO_4. Fill the beaker *B* with ice and water. Use three storage cells and secure a voltage across the terminals of about 6.75 volts and a current density of 1 amp. per square centimeter.

A copious white crystalline precipitate soon settles from the anode to the bottom of the tube *T*. After an hour or so, interrupt the process, decant the electrolyte from the crystals, collect them on a small filter in a Gooch crucible, wash them with alcohol using a pump, and dry them in air. The decanted solution may be used for another run.

Reference: Friend, II, 175; Mellor, X, 477; Elbs, *Z. Elektrochem.*, **2**, 162 (1895).

2. Preparation by the Action of H_2O_2 on Acids or Their Salts.—By this more general method, a large number of per-acids or their salts have been prepared.

EXERCISE 50. SODIUM PERBORATE, $NaBO_3 \cdot 4H_2O$

Dissolve 20 g. of borax and 4 g. of sodium hydroxide in the minimum volume of cold water and slowly add the solution to 120 cc. of a 3 per cent solution of hydrogen peroxide (the usual concentration of the reagent). Cool the solution in ice water. After a short time, small difficultly soluble crystals of sodium perborate separate. Filter the crystals and wash them with cold water, then with alcohol and ether. Dry the crystals in the air. The salt is moderately stable when well stoppered but slowly decomposes.

References: Friend, IV, 36; Mellor, V, 116; Melikoff and Pissarjewsky, *Ber.*, **31,** 953 (1898); Bruhat and Dubois, *Compt. rend.*, **140,** 506 (1905); For constitution, Tanatar, *Z. phys. Chem.*, **26,** 132 (1898); **29,** 162 (1899).

Additional Exercise: Ammonium perborate, Melikoff and Pissarjewsky, *loc. cit.*

EXERCISE 51. POTASSIUM PERCHROMATE, K_3CrO_8

In a 500-cc. flask, prepare a solution of 25 g. of potassium hydroxide in 200 cc. of water and to this add a solution of 13 g. of chromic anhydride, CrO_3, in 25 cc. of water. Cool the solution with a freezing mixture until ice begins to separate; then, with constant shaking of the flask, add drop by drop 25 cc. of a 30 per cent solution of hydrogen peroxide. It should be noticed that this is the strongest solution of hydrogen peroxide commercially available. Throughout the operation, the temperature must not rise above 0°, ice crystals being present at all times during the addition of the hydrogen peroxide. The yellowish-red solution soon changes to brownish black. After 1 to 2 hr., the crystallized salt has separated on the bottom of the flask. Decant the mother liquor, and filter the crystals with air suction. Repeatedly wash the salt with small portions of 95 per cent alcohol until the wash alcohol is no longer colored yellow by dissolved chromic acid. Then dry the crystals by washing with ether or on a porous clay plate. Preserve in a glass-stoppered bottle.

References: Friend, VII (II), 74; Mellor, XI, 356; Riesenfeld, Wohlers, and Kutch, *Ber.*, **38**, 1885 (1905).

EXERCISE 52. POTASSIUM PERVANADATE, KVO_4

Prepare 10 g. of potassium metavanadate, KVO_3, either by heating a solution of vanadium pentoxide, V_2O_5, with the necessary amount of a solution of potassium hydroxide or by boiling the necessary amount of ammonium metavanadate (difficultly soluble) with the required quantity of potassium hydroxide. In either case, obtain the white, needle-shaped crystals by evaporation.

In an excess of concentrated (30 per cent) hydrogen peroxide to which a little sulfuric acid has been added to insure acidity, dissolve the potassium metavanadate, observing that the color changes to an intense yellow. To this solution, well cooled, add 95 per cent alcohol until the pervanadate has been precipitated as a microcrystalline powder. Filter off the product, wash with alcohol, and dry in a desiccator over calcium chloride.

References: Friend, VI (III), 92; Mellor, IX, 795; Scheuer, *Z. anorg. Chem.*, **16**, 290 (1898).

VII. DISSOCIABLE COMPOUNDS

A great many compounds exert a considerable vapor pressure because of thermal dissociation, with the production of one or more gaseous components. Such is the case with efflorescent hydrates. Other examples are the compounds $(NH_4)_2S$, WCl_6, PCl_5; and many ammoniates, such as $AgCl \cdot 3NH_3$. The extent of dissociation is increased by rise of temperature and diminished by counterpressure of the gaseous product of dissociation. Some compounds require a back pressure of more than one atmosphere and can be obtained only at higher pressures. An example is phosphonium chloride, PH_4Cl. The iodide (PH_4I) can be prepared at atmospheric pressure and ordinary temperature, but it evaporates rapidly and must be preserved in sealed containers. At 20°, it has about 50 mm. vapor pressure.

References to Dissociation Pressures: Johnston, *J. Am. Chem. Soc.*, **34,** 877 (1912); Smith and Calvert, *ibid.*, **36,** 1377 (1914).

EXERCISE 53. PHOSPHONIUM IODIDE, PH_4I

Under a good hood, arrange an apparatus as represented in Fig. 17 but having a Liebig condenser and receiver instead of the air condenser *A* and the flask and wash bottles *C* and *E*. The retort *B* (150 cc.) should have a short neck, and there should be in readiness an air condenser *A*, consisting of a wide (2 cm.) glass tube of thin walls and about 50 cm. in length, joined to a distilling flask *C* and wash bottles *E*, so that it may be substituted for the Liebig condenser without loss of time. The retort may be joined to the two condensers by binding the joint with electrician's tape.

Fill the retort *B* with dry carbon dioxide, generated in *F* and dried by sulfuric acid in *G*, and then place in it 20 g. of white phosphorus, cut into small pieces under water and dried piece by piece on filter paper. Continue the current of carbon dioxide until the phosphorus is entirely dry, then add sufficient carbon disulfide to dissolve the phosphorus (about 20 cc.). Cool the retort in running water and add 34 g. of iodine gradually in small quantities and with thorough shaking after each addition.

Arrange a water bath in such a way as to immerse the solution in it and distill off the carbon disulfide as completely as possible, since its presence interferes with the next step. Quickly replace the Liebig condenser with the air condenser and its train, as shown in Fig. 17, and renew the current of dry carbon dioxide until all air has been displaced from the apparatus.

Replace the water bath by a sand bath *H* and very slowly add, through the dropping funnel *D*, about 12 cc. of water, heating the retort gently at first and then more strongly toward the end of the reaction. Phosphine, PH_3, and hydrogen iodide, HI, are evolved and in the air condenser unite to form glittering colorless crystals of phosphonium iodide, PH_4I. The condensation may be aided by covering the condenser with a cold wet towel. When no more phosphonium iodide comes over (or it begins to be colored), disconnect the air condenser, rapidly scrape out the crystals into a clean dry test tube, and seal the tube. Very beautiful crystals may be obtained by slowly subliming the compound from one end of the tube to the other, keeping the two ends at somewhat different temperatures.

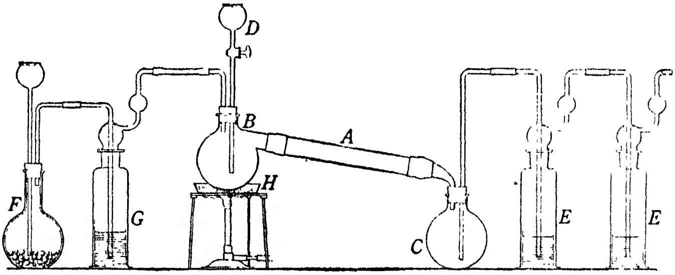


Fig. 17.—Preparation of phosphonium iodide.

Excess of hydrogen iodide is absorbed by water in *E*, while some phosphine escapes. The flask *C* serves to prevent water from sucking back into the condenser. It must be remembered that phosphine vapors mixed with air are explosive, so the apparatus must be kept full of carbon dioxide all the time.

References: Mellor, VIII, 824; Baeyer, *Ann.*, **155**, 269 (1870); Hofmann, *Ber.*, **6**, 286 (1873).

Additional Exercises: Phosphonium bromide, PH_4Br; phosphorus pentachloride, PCl_5; iodine trichloride, ICl_3.

VIII. CRYSTALLIZATION FROM SOLUTIONS CONTAINING TWO OR MORE SALTS

When two salts having a common ion are brought together in solution, and the solution is concentrated to crystallization, any one of four cases may arise:

1. The two salts may separate together, each retaining its individuality, so that each may be recognized, and the two varieties of crystals may be separated mechanically. Such a product is called a *conglomerate* or a *mixture.*

2. Each crystal may be made up of both salts but in no molecular ratio. In this case, the composition will vary with the concentration of the two salts in the original solution, and repeated recrystallization will, in general, change the composition in a regular variation. Such crystals are called *mixed crystals* and are regarded as a solution of one solid in another (Exercise 3).

3. The crystals may contain both salts in definite molecular ratio. Their solution will, however, respond to tests for all of the ions originally present. Thus, carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$, gives tests for the ions K^+, Mg^{++}, and Cl^-. Such salts are called *double salts*, and their formulas are written, as has just been illustrated, as a series of molecular formulas parted by periods.

4. The crystals may contain the two salts in molecular ratios, as in the case of double salts, but when they are

dissolved the solution gives tests for a new ion, although it may to some extent give tests for the old ones as well. Such a compound is called a *complex salt.* Thus, when potassium cyanide and cadmium cyanide are brought together, they dissolve to a clear solution which does not give a test for the CN^- ion with silver nitrate or for cadmium with ammonium hydroxide.

Both double and complex salts have many applications in the industries and in chemical work, and several typical examples of each class will now be described.

Topic: Mixed crystals and solid solutions, textbooks on physical chemistry; Friend, I, 109; Mellor, I, 658; Foote, *J. Am. Chem. Soc.*, **34,** 880 (1912); Retgers, *Z. phys. Chem.*, **5,** 461 (1890); Bruni, *Chem. Rev.*, **1,** 345 (1925).

1. Double Salts.—As a rule, a double salt is made up of two different salts of the same acid, so that we have double chlorides, double sulfates, double nitrates; and the salts of practically all acids enter into these combinations. It is usually the case that one of the salts is that of an alkali metal (including ammonium); the other, that of some metal of higher valence. Calcium, strontium, and barium do not enter into these formations so frequently as do most other metals. Less frequently, the cations are the same and the anions different, as in the salt $NaNO_3 \cdot Na_2SO_4$. The ratios in which the two salts unite are quite variable but are nearly always small ones such as 1:1, 1:2, and, less often, 2:3. Among the double halides, the number of molecules of the alkali halides which can unite with one of the elements of higher valence is usually limited by this valence, though this is not always true. For example, aluminum chloride might be expected to form the salt $AlCl_3 \cdot 3KCl$, as well as those of the ratios 1:1, 1:2, but it would not in all probability form a salt of the ratio 1:4. It is also true, in general, that the total number of halogen atoms present does not exceed six.

It will be seen that within the limits described, there is a very great range of possibility, and many hundreds of double salts have been prepared.

References: Werner, New Ideas on Inorganic Chemistry (1911); Sidgwick, The Electronic Theory of Valency (1929); Ephraim, pp. 240, 257.

Among the double salts certain types are so persistent that they deserve special attention. The following are examples:

Carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$.—A similar salt is to be expected with ammonium, rubidium, or cesium replacing potassium, zinc, cadmium, iron, nickel, cobalt, or stannous tin, replacing magnesium; and bromine and occasionally iodine replacing chlorine. Many of these are known but not all. (Mellor, II, 430.)

Mohr's Salt, $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$.—Similar salts are formed with potassium, rubidium, and cesium, replacing ammonium, magnesium, zinc, cobalt, nickel, and manganese, replacing iron.

Alum, $KAl(SO_4)_2 \cdot 12H_2O$.—Ammonium, rubidium, cesium, univalent thallium, and in some cases sodium may replace potassium, while the aluminum may be replaced by trivalent iron, chromium, indium, gallium, titanium, vanadium but not by the rare-earth metals.

References: Typical articles on double salts: Foote, *J. Am. Chem. Soc.*, **32,** 618 (1910); **33,** 459, 463, 1032 (1911); Richards and Shaw, *Am. Chem. J.*, **15,** 642 (1893); **17,** 145, 297 (1895).

Conditions for the Formation of Double Salts.—The state of a double salt in solution must be regarded as a very complex equilibrium between the double salt, its constituent simple salts, and the several ions into which the latter ionize:

$$KCl{\cdot}MgCl_2 \rightarrow KCl + MgCl_2 \rightarrow Mg^{++} + K^+ + 3Cl^+.$$

If such a system undergoes concentration at a given temperature, say 20°, that solid will begin to separate by crystallization which first reaches its saturation value. What will happen as concentration proceeds will depend upon the relation of the solubility curves of the several compounds present in the solution. A few of the simplest cases will be illustrated by diagrams.

Case I. No Double Salt Separates.—Let us suppose that the solubility of the compound *A* at a given temperature (say 20°) is represented (Fig. 18) by point *A* on the abscissa *OX*; the solubility of the compound *B*, by the point *B* on the ordinate *OY*; and let us further suppose that the two salts have a common anion, *e.g.*, are both chlorides. If to the saturated solution *A* some salt *B* is added, the common ion effect will diminish the solubility of *A*, the line *AC* representing the diminishing solubility of *A* as increasing quantities of *B* are added.

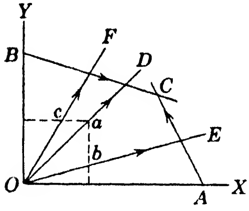


Fig. 18.

In like manner, the solubility of *B* will be decreased by the addition of *A*, and the line *BC* will represent the diminishing solubility of *B* as *A* is added to its saturated solution. Within the area *OACB*, the solution is unsaturated with any salt. If we prepare an unsaturated solution with equivalent parts of *A* and *B*, its concentration will be represented at some point *a* on the line *OD*, bisecting the angle *O*, since the coordinates of any point on this line are always equal. If a solution of concentration *a* is evaporated at constant temperature, say 20°, the point representing concentration will move toward *D*. On reaching the line *BC*, the solution is saturated with *B*, which now begins to crystallize out. This alters the relative concentration of the two salts, and the representative point moves along the line *BC* toward *C*. At this point, *A* begins to crystallize out along with *B*. On further evaporation, the solution does not change concentration but yields both salts in unchanging ratio. The point *C* is called the *end point* of crystallization. In like manner, the course of evaporation of other initial concentrations, as *b* and *c*, may be traced. It is, of course, to be understood that the curves as drawn have been determined by experiment and cannot be predicted by theoretical considerations.

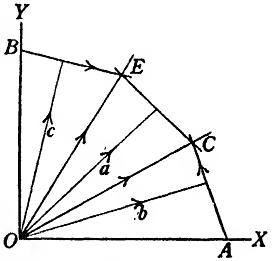


FIG. 19.

Case II. One Double Salt Forms.—Figure 19 represents the simplest case of double-salt formation in which only one double salt forms. On addition of *B* to a saturated solution of *A*, the latter salt separates as before, up to the point *C*. Here a double salt begins to crystallize out. On adding *A* to a saturated solution of *B*, the latter salt is deposited up to the point *E*, when the double salt again appears. If we start at any point of unsaturation in the area *EOC*, as at *a*, saturation will be reached on the line *EC*, which is the curve for the solubility of the double salt, and this salt will separate. Starting at any point in the area *BOE*, the compound *B* will first appear, followed by the double salt, while any point in the area *AOC* will first yield *A* and later the double salt. It will be seen that in this case the two salts do not need to be in equivalent ratio to produce the double salt but can have quite a range of concentration. If the salts are not in equal ratio, the end point will be at *E* or at *C*, depending upon which salt is in excess.

Case III. An Excess of One Component Is Necessary.—It sometimes happens that an excess of one component is requisite for the formation of a double salt. Conversely, if the solid double salt is dissolved and the solution is evaporated, one of the components separates until the required excess of the other component has accumulated in the solution. This case is well illustrated by the mineral carnallite, $KCl\cdot MgCl_2\cdot 6H_2O$, one of the products of the Stassfurt mines. Let the point *A* (Fig. 20), represent a saturated solution of potassium chloride; and the point *B*, a saturated solution of magnesium chloride. An unsaturated solution of equivalent quantities of the two salts is then represented on the line *OE*, say at *a*. If the solution is evaporated at constant temperature (20°), the point *a* approaches the solubility curve of potassium chloride, *viz.*, the line *AC*. At *E*, potassium chloride begins to separate and continues to do so until the representative point has moved to *C*, at which point carnallite makes its appearance. Since the separation of carnallite withdraws the two salts in equimolecular ratio from the solution, and since the solution now contains much more magnesium chloride than potassium chloride, the deposits of crystals of carnallite leave the solution unsaturated with respect to potassium chloride, and the latter salt steadily passes into solution again, while the deposit of carnallite increases. If, when the point *C* is reached, the crystals of potassium chloride are

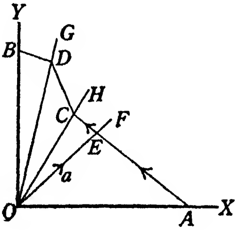


FIG. 20.

filtered off, the representative point moves along *CD* to *D* with the deposit of carnallite. At *D*, magnesium chloride appears, and *D* is the end point of crystallization. To obtain pure carnallite, we must start at some concentration within the area *DOC*.

Many other cases arise that cannot be considered here. For example, two or more double salts may form, depending upon the ratio of the salts in solution. The two salts may have no common ion, as potassium chloride and magnesium sulfate. On evaporation, either of these two or the two salts formed by their double decomposition may separate as well as any one of a number of double salts. Sometimes a double salt cannot be obtained unless the temperature is below a given point, called the transition point; while in other cases the temperature must be above the transition point. Thus, the salt known as kainite, $MgSO_4 \cdot KCl \cdot 3H_2O$, cannot be obtained above 83°; while with astrakanite, $MgSO_4 \cdot Na_2SO_4 \cdot 4H_2O$, the temperature must be above 4.5 and below 60°.

References: Van't Hoff, Bildung und Spaltung von Doppelsalzen (1897); van't Hoff, Zur Bildung der Ozeanischen Salzablagerung, I (1905), II, (1909); Findlay, The Phase Rule (1927); Hildebrand, *J. Ind. Eng. Chem.*, **10,** 96 (1918); Stewart, Some Physico-chemical Themes, Chap. IV (1922).

EXERCISE 54. FERROUS AMMONIUM SULFATE (MOHR'S SALT), $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$

Dissolve 100 g. of commercial ferrous sulfate (copperas) in 400 cc. of hot water to which has been added 1 or 2 cc. of sulfuric acid and then add an equimolecular weight of ammonium sulfate, remembering that the formula for ferrous sulfate is $FeSO_4 \cdot 7H_2O$. It is well to add a bright iron nail and keep the solution hot for a time to reduce any ferric sulfate which may be present. Bring the solution to crystallization, avoiding the formation of crystal masses. The salt crystallizes in the monoclinic system, forming large, clear crystals of a somewhat lighter shade of green than the crystals of ferrous sulfate. The salt should be carefully air dried, avoiding efflorescence, and its solution should give no test for ferric iron with potassium thiocyanate. It is used as a standard in volumetric analysis, since it is not easily oxidized, can be secured in good, weighable form, and happens to contain a convenient fraction of its weight in iron, (*viz.*, one-seventh), which simplifies calculations somewhat.

Reference: Friend, IX (II), 156.

The Preparation of Alums.—Since aluminum sulfate is a commercial chemical, the aluminum alums can be prepared by crystallizing the salt along with the double molecular weight of an alkali sulfate. Chromium and ferric sulfates are not well crystallized and have limited uses, so that they are not readily obtained. The preparation of their alums involves the preliminary preparation of the sulfates themselves.

EXERCISE 55. POTASSIUM CHROME ALUM, $KCr(SO_4)_2 \cdot 12H_2O$

This salt is prepared by the reduction of potassium dichromate in the presence of sulfuric acid, illustrating the reduction of a salt of a metallo-acid. Pour 35 cc. of concentrated sulfuric acid into 110 cc. of water and dissolve in this solution 50 g. of potassium dichromate. As a reducing agent, starch may be used (or sulfur dioxide or alcohol). Add 12 g. of starch very slowly, stirring all the time during the energetic reaction. As a rule, no external heat is required, though occasionally a little is needed to start the reaction. In any case, the temperature should not rise above about 60°, since a green insoluble basic chromium sulfate will then form. When the reaction is ended, set the solution aside to crystallize, preferably under 20°. This may require some time unless the weather is cold. The salt crystallizes in ruby-red octahedra.

References: Mellor, XI, 454; Friend, VII (III), 81; Rohrman and Taylor, *J. Chem. Educ.*, **6**, 473 (1929); Traube, *Ann.*, **66**, 169 (1848); Böttger, *J. prakt. Chem.*, **36**, 318 (1845).

EXERCISE 56. AMMONIUM IRON ALUM, $(NH_4)Fe(SO_4)_2 \cdot 12H_2O$

As a preliminary, ferric sulfate is made by the oxidation of ferrous sulfate. Dissolve 100 g. of ferrous sulfate in 100 cc. of boiling water, to which has been added before heating 10 cc. of sulfuric acid. Add concentrated nitric acid portionwise to the hot solution, until a diluted sample gives a reddish-brown (not black) precipitate with ammonia. This will require about 25 cc. Boil the solution down to a viscous liquid to get rid of excess nitric acid, dilute to about 400 cc., and add the calculated weight of ammonium sulfate. The crystallization is conducted as in the former exercise, preferably under 20°. By the addition of potassium sulfate, the corresponding potassium iron alum may be secured. In this case, it is necessary to concentrate the solution until there is about four parts of water to one of the hydrated alum and cool to about zero to secure crystallization. Both of these alums are amethyst in color, the potassium salt being much less stable and having a rather low transition point.

References: Friend, IX (II), 164; Howe and O'Neal, *J. Am. Chem. Soc.*, **20**, 759 (1898).

Additional Double Salts: (Look up commercial uses.) $(NH_4)_2SO_4 \cdot NiSO_4 \cdot 6H_2O$; $(NH_4)_2SO_4 \cdot CuSO_4 \cdot 6H_2O$; $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$; $K_2SO_4 \cdot CuSO_4 \cdot 6H_2O$; $KCl \cdot MgCl_2 \cdot 6H_2O$; $KCl \cdot FeCl_3 \cdot H_2O$; $2KCl \cdot CuCl_2 \cdot 2H_2O$; $2NH_4Cl \cdot CuCl_2 \cdot 2H_2O$.

2. Complex Salts.—Complex salts, when dissolved in water, give ions which are different from those of the original components. For example, when potassium nitrite, a cobaltic salt, and dilute acetic acid are brought together, a sparingly soluble salt forms which has the composition represented by the double-salt formula $3KNO_2 \cdot Co(NO_2)_3$. In solution, this salt gives the cation K^+ and the anion $Co(NO_2)_6^{---}$. The formula of the salt is therefore written $K_3Co(NO_2)_6$. In a similar way, we have potassium ferrocyanide, $K_4Fe(CN)_6$, and ferricyanide, $K_3Fe(CN)_6$. All of these salts enter into double decomposition with other simple salts in such a way that the potassium and the other simple cation change places, the complex anion remaining unchanged. It is even possible to prepare many of the free acids from which these salts are derived such as $H_4Fe(CN)_6$; $H_3Fe(CN)_6$; H_2PtCl_6.

The distinction between a double salt and a complex salt is really one of degree rather than of absolute difference. To some extent in very dilute solution, all complex ions may be regarded as undergoing slight ionization into simple ones; in concentrated solution, many double salts give evidence of the formation of complex ions, which decompose into simple ions as the dilution increases. Thus, the complex salt $K_2Cd(CN)_4$ in the main ionizes into $2K^+$ and $Cd(CN)_4^{--}$, but the latter ion sets up the equilibrium $Cd(CN)_4^{--} \rightleftarrows Cd^{++} + 4CN^-$ to such an extent that the cadmium is precipitated by solutions of soluble sulfides as CdS. Alum, in concentrated solutions, gives the ions $K^+ + Al(SO_4)_2^-$; while in dilute solution, the ions are $K^+ + Al^{+++} + 2SO_4^{--}$.

The formation of complex salts is particularly common when the acid radical is any one of the following: CN^-, CNS^-, $S_2O_3^{--}$, $C_2O_4^{--}$, NO_2^-; and when the metal associated with the radical is one of the following: Co^{+++}, Hg^{++}, Cd^{++}, Fe^{+++}.

EXERCISE 57. SODIUM COBALTINITRITE, $Na_3Co(NO_2)_6$

Dissolve 75 g. of sodium nitrite in 75 cc. of water heated to 45 to 50° and then add 25 g. of cobalt nitrate, stirring the mixture and maintaining the temperature until all is dissolved. Place the solution in a liter flask and add, a little at a time and with constant shaking, 13 g. of glacial acetic acid. Copious fumes of nitrogen dioxide are evolved (hood), and the cobalt is oxidized to the trivalent condition. With frequent shaking, allow the mixture to stand for half an hour and then filter from any precipitate of potassium cobaltinitrite, washing the precipitate once with a small quantity of water. If there is a considerable precipitate, add enough water to dissolve nearly all of it before filtering. Place the solution in a rather narrow bottle or gas-washing flask and draw or blow air through it for half an hour to wash out the oxides of nitrogen. Replace the solution in the large flask and slowly add 75 cc. of alcohol, shaking at frequent intervals. (Denatured alcohol is apt to give low yields and impure products.) Allow the orange-yellow precipitate to collect for about an hour or overnight and then collect on a Büchner funnel, washing first with one small portion of 60 per cent alcohol and then with small portions of 95 per cent alcohol until the filtrate is colorless. Spread the bulky crystalline precipitate on paper to dry. If an abundant precipitate fails to form, it is probable that not enough acetic acid has been added.

To a little of the filtrate from the crystals, add a solution of a potassium salt, observing the instant precipitation of the insoluble potassium cobaltinitrite. An excess added to all of the mother liquors will give a preparation of this potassium salt, mixed with a mixed salt of the composition $K_2NaCo(NO_2)_6$.

References: Mellor, VIII, 503; Friend, IX (I), 60; Biilmann, *Z. anal. Chem.*, **39,** 286 (1900); Cunningham and Perkins, *J. Chem. Soc.*, **95,** 1567 (1909); Rosenheim and Koppel, *Z. anorg. Chem.*, **17,** 43 (1898).

EXERCISE 58. SODIUM NITROPRUSSIDE, $Na_2Fe(CN)_5NO{\cdot}2H_2O$

Put 20 g. of potassium ferrocyanide in a 250-cc. Erlenmeyer flask, adding 30 cc. of water. Place the flask on the water bath and heat till the ferrocyanide dissolves. Add 35 cc. of nitric acid (sp. gr., 1.24) and continue heating until a test portion shows no blue color but a dark green precipitate when treated with ferrous sulfate. Let stand for a day or two and filter off the tarry impurities. Now neutralize with sodium carbonate, taking care that no excess is added. Warm and, when cool, add from one to two times the volume of alcohol (ethyl). Set the flask in a dry place for a day or two, after which the impurities (chiefly crystals of potassium nitrate) may be filtered off, and the nitroprusside crystallized out. Sometimes two or three treatments with alcohol are necessary. In order to expedite the operation of evaporating down to crystallization, the solution may be evaporated by heating in a suction flask under reduced pressure. Quick crystallization increases the yield. The yield should be above 75 per cent.

References: Friend, IX (II), 228; Vanino, Handbuch der präparative Chemie, Vol. I, 355 (1925); Staedeler, *Ann.*, **151,** 1 (1869); Weith, *Ann.*, **147,** 312 (1868); Manchot, *Ber.*, **45,** 2869 (1912); **46,** 3514 (1913).

Some Complex Salts of Frequent Reference or Use:

$K_3Fe(CN)_6$, used to test for ferrous ions.

$K_4Fe(CN)_6$, used to test for ferric ions.

$K_3Fe(CNS)_6$, obtained in test for ferric ions.

$NaAg_3(S_2O_3)_2$, formed in developing photographic plates.

$K_4Fe(C_2O_4)_2$, used as a reducing agent in photography.

$K_3Co(NO_2)_6$, the precipitate obtained with DeKoenig's solution.

$KCu(CN)_2$, produced in separation of Cu and Cd.

$K_2Cd(CN)_4$, produced in separation of Cu and Cd.

3. Fluoacids and Chloroacids. When the fluoride of an alkali metal is dissolved in a solution of a fluoride of a nonmetal or of a metallo-acid element, very stable compounds of the two result which are to be regarded as salts of complex fluoacids. In a similar way are formed salts of chloroacids. Some familiar examples of such salts are the following: K_2SiF_6; K_2TiF_6; K_2ZrF_6; K_2PtCl_6; K_2TaF_7; $(NH_4)_2SnCl_6$; $KAuCl_4$. In general, potassium salts of this class are apt to be rather sparingly soluble and well crystallized, while sodium salts are much more soluble and less well crystallized. Many of the salts of heavier metals are insoluble or nearly so.

In some cases, the free acids are easily obtained, at least in solution, the following being examples: H_2SiF_6; H_2PtCl_6; $HAuCl_4$. The last two are prepared by dissolving platinum or gold in aqua regia and evaporating to crystallization. The former is obtained by the action of silicon tetrafluoride, SiF_4, on water.

References on Fluosalts: Hall, *J. Am Chem Soc.*, **26,** 1235 (1904); Ephraim and Barteczko, *Z anorg Chem*, **61,** 259 (1909); Remsen, *Am Chem. J*, **11,** 305 (1889).

EXERCISE 59. FLUOSILICIC ACID, H_2SiF_6

Select an old flask *A* (Fig. 21) of about 1 l. capacity (it will be etched in the experiment) and place in it a mixture of 50 g. of powdered fluorspar and 50 g. of fine sand. Provide the flask with a stopper carrying a funnel tube *B* and a rather wide delivery tube *C*, extending about 30 cm. in a horizontal direction and then an equal distance downward. Place the flask on a sand bath *D* that can be heated with a Bunsen burner. Arrange a 1-l. beaker *E* in such a way that the delivery tube will reach just to the bottom of the beaker. Half fill a small beaker or a crucible *F* with mercury, put it in the empty beaker, and adjust the delivery tube so that it just dips under the surface of the mercury. Then fill the beaker with pure water. Pour about 250 cc. of concentrated sulfuric acid over the mixture in the flask in portions at a time, shaking the flask so as thoroughly to wet the mixture with the acid. Place the flask on the sand bath, adjust the stopper and the safety tube, and gently warm the mixture. Silicon tetrafluoride is formed and escapes through the delivery tube, bubbling through the mercury in the small vessel. On coming into contact with the water in the beaker, a reaction occurs as follows:

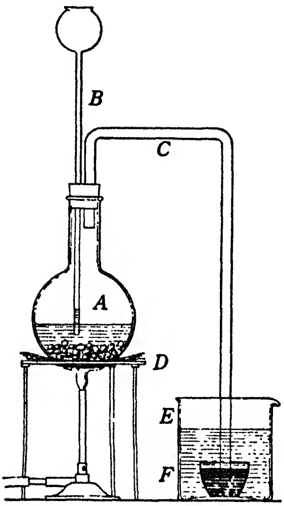


Fig. 21.—Preparation of fluosilicic acid.

$$SiF_4 + 4H_2O \rightarrow Si(OH)_4 + 4HF,$$
$$Si(OH)_4 + 6HF \rightarrow H_2SiF_6 + 4H_2O.$$

The excess of silicic acid is deposited as a gelatinous precipitate which would easily stop up a narrow delivery tube. It is to prevent this that the mercury trap is used. Continue the heating as long as the silicic acid increases; then filter through cloth and finally through paper. The product is a solution of fluosilicic acid.

Heat a portion of the solution to boiling and neutralize it with potassium carbonate. On cooling, the potassium fluosilicate separates as a very transparent crystalline product, which should be filtered off and preserved. It will serve just as well to add potassium chloride, since potassium fluosilicate is not decomposed by hydrochloric acid.

References: Friend, V, 192; Mellor, VI, 934; Berzelius, *Pogg. Ann.*, **1**, 169 (1824); Jacobson, *J. Phys. Chem.*, **27**, 761 (1923).

EXERCISE 60. POTASSIUM FLUOTITANATE, $K_2TiF_6 \cdot H_2O$

Heat to redness 25 g. of rutile and drop it into cold water (to crack the crystals). Dry it and grind it to fine powder. Or start with an equivalent quantity of titanium oxide, procurable from any good paint dealer. Mix it with twice its weight of potassium carbonate and fuse the mixture in a platinum crucible supported within a thin-walled clay crucible. When it is thoroughly fused, cool the fusion, powder it, and dissolve it in hot dilute hydrofluoric acid, avoiding much excess of the latter. Heat to boiling to dissolve all the salt, adding much water if necessary. Filter while boiling hot, using glass vessels if excess of hydrofluoric acid has been avoided. On cooling, most of the potassium fluotitanate separates in shining scales, filling the solution. Again filter with the water pump, pressing the crystals together on the filter and washing them a few times with ice-cold water. Finally, recrystallize from boiling water and dry on paper. If crystals are formed in large excess of hydrofluoric or hydrochloric acid, they are anhydrous. The hydrate loses water when dried above 100°.

References: Friend, V, 238; Mellor, VII, 71; Wöhler, *Ann.*, **74,** 212 (1850); Marchetti, *Z. anorg. Chem.*, **10,** 66 (1895); Weiss and Kaiser, *ibid.*, **65,** 354 (1910).

Additional Exercise: Potassium fluozirconate from crude zirconium oxide.

EXERCISE 61. CHLOROSTANNIC ACID, $H_2SnCl_6 \cdot 6H_2O$

A weighed quantity of anhydrous stannic chloride, $SnCl_4$, is treated with six equivalents of water in the form of a concentrated solution of hydrochloric acid. The proportions required are 100 parts of $SnCl_4$ and 41.64 parts of water, corresponding to 60.15 parts of 33 per cent hydrochloric acid of sp. gr. 1.166.

In this connection, it is well to know that the percentage of HCl in an aqueous solution is very readily calculated from the specific gravity. The decimal portion of the latter value is multiplied by 2, and the decimal point moved two places to the right. Thus, if the specific gravity is 1.166, the solution will contain 166 × 2 = 33.2 per cent HCl by weight. A simple calculation will therefore enable the student to determine the weight of hydrochloric acid to be added of any convenient density, in order to supply the requisite water.

Place about 25 g. (accurately weighed) of stannic chloride in a flask of suitable size and add the requisite weight of concentrated hydrochloric acid in small portions at a time, working under a good hood. Provide the flask with a stopper furnished with a tube for gas delivery (reaching to the bottom of the flask) and one for exit. Conduct a rapid current of dry hydrogen chloride into the solution, gently shaking the flask to promote absorption. When no more gas is absorbed, cool the flask by immersing it in ice water. The entire contents should solidify to a mass of crystals of the composition $H_2SnCl_6 \cdot 6H_2O$, which melt at 19.2°. If the experiment is successful, melt the crystals, transfer the liquid to a sealing tube, and seal.

The salts of chlorostannic acid are more easily prepared. It is necessary only to bring together in solution the calculated quantity of crystallized stannic chloride, $SnCl_4 \cdot 5H_2O$, and of the chloride of the other metal. Potassium chlorostannate, K_2SnCl_6, and ammonium chlorostannate (pink salt), $(NH_4)_2SnCl_6$, are both well-crystallized, anhydrous salts, crystallizing in octahedra. Bromostannic acid, $H_2SnBr_6 \cdot 8H_2O$, can be prepared in an entirely analogous way.

References: Friend, V, 348; Mellor, VII, 447; Seubert, *Ber.*, **20**, 793 (1887); Smith, *Z. anorg. allgem. Chem.*, **176**, 155 (1928).

Additional Exercise: Bromostannic acid, $H_2SnBr_6 \cdot 8H_2O$, Seubert, *loc. cit.*

IX. THE POLYACIDS AND THEIR SALTS

When two or more oxygen acids are brought together in the presence of a limited amount of a base, it frequently happens that a salt crystallizes which, in addition to the base, contains both acid radicals, usually in very unequal ratio. The most familiar salt of this kind is ammonium phosphomolybdate the formula of which is usually written $3(NH_4)_2O \cdot P_2O_5 \cdot 22MoO_3 \cdot 12H_2O$. The acid anhydrides which most frequently enter into these complexes are P_2O_5, As_2O_5, I_2O_5, Cb_2O_5, MoO_3, WO_3, VO_2, MnO_2. Sometimes as many as four different acids are present. Even when only two are present, 10 or 12 different salts may be formed according to conditions, and it is impossible in many cases to give directions which can be relied upon to produce a certain definite salt. For a description of the simplest of these salts, the student should consult the papers of Wolcott Gibbs in the first seven volumes of the *American Chemical Journal* and those of E. F. Smith and his pupils in the *Journal of the American Chemical Society.*

References: Middleton, *J. Chem. Educ.*, **10,** 726 (1933); Ephraim, p. 434.

EXERCISE 62. PHOSPHOMOLYBDIC ACID, $H_3PO_4 \cdot 12MoO_3 \cdot 12H_2O$

Prepare ammonium phosphomolybdate in accordance with the directions for preparing the corresponding potassium salt (Exercise 63). Dry the yellow salt and place it in a casserole together with a large excess of aqua regia. Arrange the casserole over an empty iron dish, so that by heating the latter the casserole is heated by hot air. The salt will then decompose without spattering by the escaping gases. If necessary to add more aqua regia, allow the contents of the casserole to settle out and pour off the supernatant liquid, carefully preserving it. The fresh acid may then be added, and the process repeated, the operation being a slow one. When all ammonia has been entirely destroyed, the liquid is evaporated until excess of acid has disappeared. On standing, bright yellow crystals are obtained from the very concentrated solution. From pure water, the acid crystallizes (with some decomposition) with 24 molecules of water.

References: Friend, VII (III), 164; Mellor, XI, 601; Gibbs, *Am. Chem. J.*, **3,** 320 (1881); Rosenheim and Jänicke, *Z. anorg. allgem. Chem.*, **100,** 304 (1917).

EXERCISE 63. POTASSIUM PHOSPHOMOLYBDATE, $2K_2O \cdot P_2O_5 \cdot 24MoO_3 \cdot 4H_2O$

Weigh out 12 g. of MoO_3 and 1 g. of K_2CO_3 and dissolve together by boiling in 200 cc. of water. Add 1 g. of potassium phosphate and an excess of nitric acid and place on the hot plate. A bright yellow crystalline precipitate of the potassium salt is obtained, closely resembling the ammonium salt in appearance. (For list of similar salts, see Gibbs, *Am. Chem. J.*, **3,** 325, 408 (1881); Friend, VII (III), 164; Mellor, XI, 663.)

EXERCISE 64. AMMONIUM ARSENITUNGSTATE, $3(NH_4)_2O \cdot As_2O_5 \cdot 24WO_3 \cdot 12H_2O$

This salt is moderately soluble in water, and to prepare it the solution must be kept concentrated at all times. Prepare a concentrated solution of eight molecules of sodium tungstate, $Na_3WO_4 \cdot 2H_2O$ (or the equivalent weight of WO_3 dissolved in sodium hydroxide). Add one molecule of sodium arsenate and neutralize the solution with concentrated hydrochloric acid. Add a considerable quantity of solid ammonium chloride and heat the solution to boiling. At first, the solution is clear, but it becomes cloudy and deposits a heavy white precipitate. Allow it to cool; filter off the precipitate; and wash it, first with a little of a solution of ammonium chloride acidulated with hydrochloric acid, then with a very little pure water. Dry the product on filter paper. The yield is not very good, owing in part to the solubility of the salt.

References: Friend, VII (III), 256; Mellor, IX, 132; Kehrmann and Rüttemann, *Z. anorg. Chem.*, **22,** 285 (1900); Rosenheim and Jänicke, *ibid.*, **101,** 268 (1917).

EXERCISE 65. AMMONIUM PHOSPHO-VANADIOTUNGSTATE, $13(NH_4)_2O \cdot 2P_2O_5 \cdot 8V_2O_5 \cdot 34WO_3 \cdot 86H_2O$

Bring together in a liter flask 1 g. of ammonium phosphate, 15 g. of ammonium tungstate, 3 g. of ammonium vanadate, 20 cc. of ammonium hydroxide, and 700 cc. of water. The ammonium tungstate and vanadate may be prepared from the corresponding anhydrides WO_3 and V_2O_5, which are more available.

Boil the solution for about 6 hr. At first, the solution is colorless but soon changes to yellow and then to red, and to this point the ammonium tungstate dissolves very rapidly. Filter off the slight residue, evaporate to a density of 1.115, and allow to stand overnight. Evaporate the mother liquor for a second crop. The crystals are dark red in color and are octohedra or cubes in form.

References: Mellor, IX, 835; Friend, VII (III), 258; Rogers, *J. Am. Chem. Soc.*, **25,** 299 (1903).

EXERCISE 66. AMMONIUM PHOSPHO-VANADICO TUNGSTATE, $15(NH_4)_2O \cdot 2P_2O_5 \cdot 6V_2O_3 \cdot 44WO_3 \cdot 106H_2O$

In a liter flask, bring together 1 g. of ammonium phosphate; 15 g. of ammonium tungstate; 1.1 g. of vanadium trioxide, V_2O_3; 25 cc. of ammonia; and 700 cc. of water. Prepare the V_2O_3 by heating 1.6 g. of ammonium vanadate (or V_2O_5) with concentrated hydrochloric acid and evaporating on the hot plate to dryness. Boil the mixture for about 6 hr., by which means a nearly black solution will be obtained. Evaporate to a density of 1.030 and allow to stand overnight. The crystals are black and show the faces of octahedra and cubes.

References: Mellor, IX, 836; Rogers, *J. Am. Chem. Soc.*, **25,** 303 (1903)

X. THE ACTION OF WATER AND OF AMMONIA UPON METALLIC SALTS

To understand the action of ammonia on metallic salts, it is necessary to have in mind the close parallel in properties between water and liquid ammonia. They are the most general solvents for metallic salts, both having great ionizing power. They have high dielectric constants, high freezing points and boiling points (compared with other hydrides of acid-forming elements), and high heats of vaporization and liquefaction. With metals, they act in analogous ways:

$$\begin{aligned} 2K + 2HOH &\rightarrow 2KOH + H_2; \\ 2K + 2HNH_2 &\rightarrow 2KNH_2 + H_2; \\ Mg + H_2O &\rightarrow MgO + H_2, \\ 3Mg + 2NH_3 &\rightarrow Mg_3N_2 + 3H_2. \end{aligned}$$

In these and in many other reactions, the ion OH^- is analogous with NH_2^-.

When a salt is exposed to either water or ammonia (as vapor or as liquid) or to a mixture of the two, the reaction that takes place may be due to any of the following: H_2O, NH_3, the ions OH^- or NH_2^-, or the ions of NH_4OH. These possibilities lead to the following types of reactions:

1. Double decomposition by NH_4OH. A metallic hydroxide may precipitate, insoluble in excess of ammonium hydroxide or ammonium salts. Examples in analytical chemistry are the precipitation of the hydroxides of iron and aluminum

$$FeCl_3 + 3NH_4OH \rightarrow Fe(OH)_3 + 3NH_4Cl.$$

2. Formation of ammonates or hydrates. Many salts when exposed to moist air take up water to form *hydrates*, thus:

$$CaCl_2 + 6H_2O \rightarrow CaCl_2 \cdot 6H_2O.$$

In a similar way, many salts in an atmosphere of ammonia take up ammonia to form *ammonates*, thus:

$$\begin{aligned} CaCl_2 + 8NH_3 &\rightarrow CaCl_2 \cdot 8NH_3 \\ 2AgCl + 3NH_3 &\rightarrow 2AgCl \cdot 3NH_3 \\ 2AgCl \cdot 3NH_3 + 3NH_3 &\rightarrow 2(AgCl \cdot 3NH_3). \end{aligned}$$

Many of these ammonates effloresce in air as do hydrates and recover ammonia from an atmosphere of that gas.

References: Franklin, The Nitrogen System of Compounds (1935); Fernelius and Johnson, *J. Chem. Educ.*, **5**, 664, 828 (1928); Findlay, The Phase Rule, 6th ed., p. 76 (1927).

Hydrates are more often obtained by crystallizing salts from water and are very familiar compounds. A large number of salts are soluble in liquid ammonia, and from that solvent they usually crystallize as ammonates.

Many salts when treated with a mixture of water and ammonia, NH_4OH, give at first a precipitate of the metallic hydroxide, which then dissolves in an excess of the reagent, indicating the formation of a complex ion, and it has been found that this complex ion consists of the original cation together with two, four, or six molecules of ammonia. Among these salts are those of silver, zinc, copper, chromium, nickel, cobalt, and the platinum metals. Crystallization from such solutions yield a great variety of ammonates such as the following:

$$\begin{array}{rl} Ag(NH_3)_2Cl; & Cu(NH_3)_4Cl_2; \\ Cu(NH_3)_2Cl; & Zn(NH_3)_4SO_4; \\ Co(NH_3)_6(NO_3)_3; & Pt(NH_3)_6Cl_4; \\ Ni(NH_3)_6SO_4; & Os(NH_3)_6(NO_3)_4. \end{array}$$

These ammonates differ in some respects from those obtained in the other two ways and have been extensively investigated by Werner. He calls them ammino salts and writes their formulas in the way just indicated. In naming them, he indicates the number of ammonia groups by Latin numerals, thus: hexammino-cobalti nitrate = $Co(NH_3)_6(NO_3)_3$; just as we similarly name the hydrate $CaCl_2{\cdot}6H_2O$ hexahydrocalcium chloride.

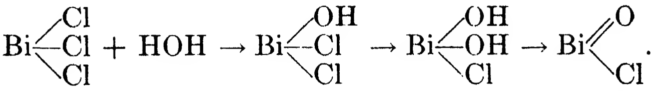
Werner has developed an elaborate structural conception of these ammino salts.

References: Werner: New Ideas on Inorganic Chemistry (1911); Friend, Vol. X, entire; Schwartz; The Chemistry of the Inorganic Complex Compounds (trans. by Bass, 1923).

To E. C. Franklin, these compounds are merely the analogues of hydrates which are more stable than ordinary hydrates. It is probable that the metallic cations in aqueous solutions are also complexes with water molecules but not so stable as with ammonia.

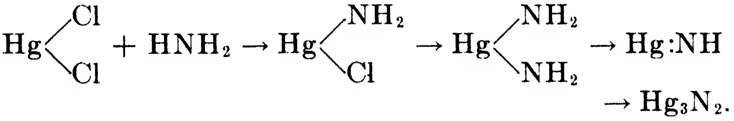
References: Franklin, *loc. cit.*; Fernelius and Johnson, *loc. cit.*

3. Ammono basic salts. It will be recalled that with water a salt frequently undergoes hydrolysis, as illustrated in the series



$$\mathrm{Bi}\begin{array}{l}\diagup \mathrm{Cl}\\ -\mathrm{Cl}\\ \diagdown \mathrm{Cl}\end{array} + \mathrm{HOH} \rightarrow \mathrm{Bi}\begin{array}{l}\diagup \mathrm{OH}\\ -\mathrm{Cl}\\ \diagdown \mathrm{Cl}\end{array} \rightarrow \mathrm{Bi}\begin{array}{l}\diagup \mathrm{OH}\\ -\mathrm{OH}\\ \diagdown \mathrm{Cl}\end{array} \rightarrow \mathrm{Bi}\begin{array}{l}\diagup\!\!\diagup \mathrm{O}\\ \\ \diagdown \mathrm{Cl}\end{array}.$$

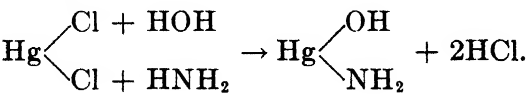
Ammonia acts in a very similar way upon salts of mercury:



$$\mathrm{Hg}\begin{array}{l}\diagup \mathrm{Cl}\\ \diagdown \mathrm{Cl}\end{array} + \mathrm{HNH_2} \rightarrow \mathrm{Hg}\begin{array}{l}\diagup \mathrm{NH_2}\\ \diagdown \mathrm{Cl}\end{array} \rightarrow \mathrm{Hg}\begin{array}{l}\diagup \mathrm{NH_2}\\ \diagdown \mathrm{NH_2}\end{array} \rightarrow \mathrm{Hg{:}NH} \rightarrow \mathrm{Hg_3N_2}.$$

This kind of a reaction has been called *ammonolysis* because of its close analogy with hydrolysis.

4. Simultaneous hydrolysis and ammonolysis. It is possible for a salt to undergo simultaneous hydrolysis and ammonolysis, which will be readily understood from the equations



$$\mathrm{Hg}\begin{array}{l}\diagup \mathrm{Cl} + \mathrm{HOH}\\ \diagdown \mathrm{Cl} + \mathrm{HNH_2}\end{array} \rightarrow \mathrm{Hg}\begin{array}{l}\diagup \mathrm{OH}\\ \diagdown \mathrm{NH_2}\end{array} + 2\mathrm{HCl}.$$

It will also be remembered that sometimes a simple base undergoes a partial dehydration, as indicated in the reaction

$$\mathrm{HO{-}Pb{-}OH + HO{-}Pb{-}OH \rightarrow HO{-}Pb{-}O{-}Pb{-}OH + H_2O.}$$

In a similar way, condensation of the mixed ammonia-water bases of mercury may take place, with loss either of water or of ammonia.

$$\mathrm{NH_2{-}Hg{-}OH + HO{-}Hg{-}NH_2 \rightarrow NH_2{-}Hg{-}O{-}Hg{-}NH_2 + H_2O,}$$

$$\mathrm{HO{-}Hg{-}NH_2 + NH_2{-}Hg{-}OH \rightarrow HO{-}Hg{-}NH{-}Hg{-}OH + NH_3.}$$

Evidently, a large variety of compounds is possible from such reactions, and many examples are known.

For further information concerning these types of compounds, together with a list of known examples, the student should consult the following references:

References: E. C. Franklin, *J. Am. Chem. Soc.*, **27**, 820 (1905); **29**, 35 (1907); **46**, 2137 (1924); *Am. Chem. J.*, **47**, 285, 361 (1912); *Proc.* 8th *Int. Cong. Appl. Chem.*, **6**, 119 (1912); Fernelius and Johnson, *J. Chem. Educ.*, **6**, 664, 828 (1928).

Preparation of Ammonia Derivatives of Metallic Salts.—The principles just described will now be illustrated by directions for the preparation of some typical salts.

1. Ammonates—Analogues of Hydrates.

EXERCISE 67. TETRAMMINO-CUPRI-SULFATE, $Cu(NH_3)_4SO_4 \cdot H_2O$

Finely powder 50 g. of copper sulfate and dissolve it by continued shaking in a mixture of 75 cc. of concentrated ammonia water and 50 cc. of water. While vigorously stirring the solution, drop into it very slowly from a dropping funnel 75 cc. of alcohol. Collect the precipitate of deep purple-blue crystals on a suction filter, pump off the mother liquor, and dry the crystals over lime in a desiccator. The addition of the alcohol is a common device to bring about the crystallization of metallic salts which cannot be evaporated. The result is due to the fact that few metallic salts are appreciably soluble in alcohol.

References: Friend, X, 29; Mellor, III, 253; Horn and Taylor, *Am. Chem. J.*, **32,** 261 (1904); Horn, *ibid.*, **38,** 475 (1907); Dawson, *J. Chem. Soc.*, **89,** 1666 (1906).

Cobaltiammine Salts.—While very few simple cobaltic salts are known, a great many complex ones have been described among which the ammino salts are the most common. It is a general characteristic of these salts that the cobalt atom surrounds itself with, or *coordinates*, six molecules or atoms of some kind to constitute a complex cation. In the salt $Co(NH_3)_6Cl_3$, the cation is $Co(NH_3)_6^{+++}$, the three chlorine atoms constituting the anions. In the salt $Co(NH_3)_5Cl_3$, only two of the chlorine atoms are ions, the third being coordinated with the five NH_3 molecules to give $Co(NH_3)_5Cl^{++}$ and $2Cl^-$. In the salt $Co(NH_3)_4Cl_3$, the ions are $Co(NH_3)_4Cl_2^+$ and Cl^-.

Formerly, these types of salts were distinguished by names which indicated color, such as purpureo, roseo, luteo, xantho. The present mode consists in designating the coordinated groups by a name ending in the suffix -ato for acid groups and -ino for basic ones, the remainder of the name being in accord with the usual custom. In accordance with this usage, the names of the three salts referred to above are hexammino-cobalti chloride; chloro-pentammino-cobalti chloride; dichloro-tetrammino-cobalti chloride.

References: Friend, X, 128–187; Werner, New Ideas on Inorganic Chemistry (1911); *Z. anorg. Chem.*, **3**, 267 (1893); *Ber.*, **40**, 15, 2103 (1907); *Z. angew. Chem.*, **19**, 1346 (1906).

EXERCISE 68. CARBONATO-TETRAMMINO-COBALTI NITRATE $[Co(NH_3)_4CO_3]\ NO_3 \cdot \frac{1}{2}H_2O$

Prepare a solution of 50 g. of ammonium carbonate in 250 cc. of water by finely powdering the carbonate and shaking it in the cold water until it has dissolved. To this, add 125 cc. of concentrated ammonia and then 25 g. of cobalt nitrate. The solution is at first deep blue. Place it in a ½-l. flask and draw through it a current of air by means of a water pump for about 3 hr., during which time the color will change to deep red. Evaporate the solution to about 150 cc., slowly adding 3 g. of solid ammonium carbonate about every 15 min. until 20 g. has been added. Filter from any suspended matter and evaporate further to 100 cc., adding 5 g. more of ammonium carbonate. Set aside to cool. Filter off the carmine-red crystals, washing them with a little water and then with alcohol. A second crop may be obtained by adding alcohol to the mother liquor.

References: Friend, X, 157; Jörgensen, *Z. anorg. Chem.*, **2**, 282 (1892); Werner, Müller, Klein and Bräunlich, *Z. anorg. Chem.*, **22**, 91 (1900).

EXERCISE 69. CHLORO-PENTAMMINO-COBALTI CHLORIDE $[Co(NH_3)_5Cl]Cl_2$

Substituting cobalt chloride for the nitrate, proceed as in Exercise 68, following the directions until the oxidation is complete and a deep red solution is obtained. Add 5 g. of ammonium chloride and evaporate the solution to a syrup. Then add dilute hydrochloric acid to decompose all carbonate and saturate the solution with ammonia gas to decompose any tetrammine salt that may be present. Add an excess of concentrated hydrochloric acid and allow the solution to cool. The salt separates in carmine-red crystals. These should be washed with alcohol. This salt was one of the first of this class to be prepared and was called purpureo-cobaltic chloride.

References: Friend, X, 146; Sörensen, *Z. anorg. Chem.*, **5**, 369 (1894); Harkins, Hall, and Roberts, *J. Am. Chem. Soc.*, **38**, 2646 (1916).

EXERCISE 70. TRINITRITO-TRIAMMINO-COBALT, $Co(NH_3)_3(NO_2)_3$

This compound is a nonelectrolyte. According to Werner, all six groups are coordinated around the cobalt atom.

Prepare a cold solution of 27 g. of sodium nitrite and 20 g. of ammonium chloride in 150 cc. of water and to this add a solution of 18 g. of crystallized cobalt chloride in 50 cc. of water. To the solution so obtained, add 100 cc. of concentrated ammonium hydroxide (20 per cent). Through this solution, draw a rapid current of air for about 3 hr. to oxidize the cobalt, by which time it should be brown in color and somewhat viscous. Pour the solution into an evaporating dish and set it aside in the open air under a hood for three or four days. Filter off by suction the crystals that have been slowly depositing and wash them with successive portions of cold water until the filtrate no longer gives a test for chloride ion.

Dissolve the impure crystals in about 400 cc. of hot water to which a little acetic acid has been added and then allow the solution to become thoroughly cold. The yellow or brown crystals are quite pure.

References: Friend, X, 162; Jörgensen, *Z. anorg. Chem.*, **17**, 475 (1898); for conductivity, Werner and Miolati, *Z. phys. Chem.*, **21**, 227 (1896).

EXERCISE 71. HEXAMMINO-CHROMIC NITRATE, $[Cr(NH_3)_6](NO_3)_3$; CHLORO-PENTAMMINO-CHROMIC CHLORIDE, $[Cr(NH_3)_5Cl]Cl_2$

a. The Hexammino Salt.—To 200 cc. of *liquid ammonia* contained in an open Dewar vessel, add 8 g. of finely powdered anhydrous chromic chloride (Exercise 29) in small portions at a time. Slow addition is necessary to prevent ammonia from boiling out of the vessel. A pink solution is obtained together with a pinkish-brown precipitate. Set the Dewar vessel aside until the excess of ammonia has evaporated (overnight). If liquid ammonia is not available, gaseous ammonia may be condensed on the anhydrous chromic chloride by cooling the containing vessel with carbon dioxide snow ("dry ice") and ether.

Add 30 cc. of ice-cold water to the residue in the Dewar vessel and, by repeated use of the same water, bring all of the solid contents as well as the water solution into a small beaker. Break up any solid lumps with a spatula and filter, washing the undissolved solid with small portions of cold water until the filtrate is no longer reddish-brown but pink and saving all the wash water combined with the first filtrate. Save also the solid matter on the filter.

To the united filtrate add concentrated nitric acid, precipitating the hexammino salt (formerly called luteochromic nitrate). Filter off this salt, dissolve it in a little warm water to which a few drops of nitric acid has been added, and again precipitate the crystalline hexammino-chromic nitrate by the addition of nitric acid and by cooling. The yield is about 7 g.

References: Friend, X, 81; Mellor, XI, 476; for technique of manipulating liquefied gases, Johnson and Fernelius, *J. Chem. Educ.*, **6**, 441 (1929); Booth, *ibid.*, **7**, 1260 (1930).

b. The Pentammino Salt.—The pink solid residue from the ice-water extraction consists of chlorò-pentammino-chromic chloride (formerly called chloropurpureo-chromic chloride). Heat this residue with concentrated hydrochloric acid a little short of boiling; cool; dilute to one and one-third volume; filter; and wash the solid with a little cold water, discarding the filtrate. Dissolve the solid salt as quickly as possible at 50° in 400 to 500 cc. of water containing a few drops of sulfuric acid. At once filter the solution as rapidly as possible (by suction) and to the filtrate add an equal volume of concentrated hydrochloric acid. Allow the red crystals that separate to stand for an hour in contact with the mother liquor; then drain them and wash them first with one part of concentrated hydrochloric acid and one part of water, then with alcohol, finally drying them in a desiccator. Yield is about 5 g.

References: Friend, X, 95; Mellor, XI, 410.

To convert the hexammino nitrate into the pentammino chloride, mix a solution of the hexammino nitrate dissolved in eleven times its weight of hot water with an equal volume of concentrated hydrochloric acid and boil gently for 30 min. to 1 hr. Cool the solution, filter off the precipitated chloro-pentammino-chromic chloride, and wash and dry as above.

References: Christensen, *Z. anorg. Chem.*, **4**, 229 (1893); to prepare chloro-pentammino-chromic chloride without the use of liquid ammonia, Christensen, *J. prakt. Chem.*, (2) **23**, 54 (1881); Jörgensen, *J. prakt. Chem.*, (2) **20**, 105 (1879).

EXERCISE 72. FÙSIBLE WHITE PRECIPITATE, $HgCl_2 \cdot 2NH_3$

The formula of this salt was formerly written Hg-$(NH_3Cl)_2$, which represents it to be a derivative of ammonium chloride; also, $Hg_2NCl \cdot 3NH_4Cl$; and it was named mercuridiammonium chloride. Dissolve 15 g. of mercuric chloride in the necessary quantity of hot water. Prepare also a solution of 25 g. of ammonium chloride in 200 cc. of aqua ammonia (1:1) and heat to boiling in a good hood. Drop the mercuric chloride into the boiling solution as long as the precipitate continues to redissolve; then set aside to cool. Small crystals of the fusible precipitate are formed as the solution cools. By filtering these off and adding additional ammonia to the filtrate, more mercuric chloride may be dissolved as before. The precipitate should be filtered off and dried on paper.

References: Friend, X, 54; Mellor, IV, 786, 846; Mitscherlich, *J. prakt. Chem.*, **19**, 453 (1840); Francois, *Compt. rend.*, **188**, 1500 (1929); Franklin, The Nitrogen System of Compounds (1935).

2. Ammono Basic Salts.

EXERCISE 73. INFUSIBLE WHITE PRECIPITATE, $Hg(NH_2)Cl$

This salt was formerly named mercuriammonium chloride. Prepare a solution of 10 g. of mercuric chloride and to this slowly add a dilute solution of ammonium hydroxide as long as a precipitate is produced, avoiding an excess. Collect the precipitate on a filter, washing it once or twice with water. Too much washing is to be avoided, since the salt turns yellow from hydrolysis. Dry the precipitate on porous paper.

References: Friend, X, 54; Mellor, IV, 786; Kane, *Phil. Mag.*, **8**, 495 (1836); **11**, 428, 504 (1837); Ullgren, *Ann.*, **26**, 205 (1838).

3. Mixed Aquoammono Base.

EXERCISE 74. MILLON'S BASE, $HO\text{-}Hg\text{-}NH\text{-}Hg\text{-}OH \cdot H_2O$

Prepare a solution of 25 g. of mercuric chloride in 200 cc. of water and heat to 70°. To this, add a solution of 7.5 g. of sodium hydroxide in 20 cc. of water. Purify the precipitate by repeated decantation and washing at the filter pump. Meanwhile, prepare some carbonate-free ammonia by treating 150 cc. of concentrated ammonia with 20 g. of lime and distilling into a receiver containing 100 cc. of water. Put the precipitate into this solution and allow it to stand, with frequent shaking, for two days in a dark place. Filter; wash with water, then with alcohol, and finally with ether; and dry at room temperature.

References: Friend, X, 54; Mellor, IV, 787, 792; Millon, *Ann. chim. phys.*, (3) **18,** 397 (1846); Holmes, *J. Chem. Soc.*, **113,** 74 (1918).

Salts of Millon's Base.—Suspend a little of the base in water and shake with a dilute solution of potassium iodide. The solution turns alkaline. The brown precipitate is the same as that produced by Nessler's solution in tests for ammonia.

XI. THIO SALTS

A large number of salts are known which are collectively designated as thio or sulfo salts. These may be classified in various ways, and several types will be described in the following exercises.

1. Salts Analogous to Well-known Oxygen Salts.—The great majority of the common oxygen acids may have a part or all of their oxygen replaced by sulfur, yielding thio acids. This includes sulfates, carbonates, phosphates, acetates, arsenates, and many others. In general, their salts are much more stable than are the free acids. These salts are formed by the union of a metallic sulfide with a nonmetallic sulfide; by boiling the salt of a lower acid with sulfur; or by treating an oxygen salt with phosphorus pentasulfide.

EXERCISE 75. POTASSIUM TRITHIOCARBONATE, K_2CS_3

Prepare 50 cc. of a 5 per cent solution of potassium hydroxide. Divide this into two equal parts; *saturate* the one with hydrogen sulfide and add it to the other. This gives a solution of potassium sulfide. Place the solution in a small flask, add 2 cc. of carbon disulfide, and shake thoroughly for some time. After about 5 min., filter through a wet filter. The orange-red solution contains K_2CS_3 and is a very sensitive reagent toward nickel. Make tests especially in the presence of cobalt.

References: Mellor, VI, 122; Friend, II, 184; Berzelius, *Pogg. Ann.*, **6**, 450 (1826); Yeoman, *J. Chem. Soc.*, **119**, 46 (1921).

EXERCISE 76. BARIUM TRITHIOCARBONATE, $BaCS_3$

The barium salt is easier to obtain in solid form than is the corresponding potassium salt. Dissolve 15 g. of crystallized barium hydroxide in 50 cc. of warm water and divide the solution into two equal parts. Completely saturate the one portion (in a stoppered flask) with hydrogen sulfide and then add the other portion, thus forming a solution of barium sulfide. Add about 1 cc. of carbon disulfide and shake from time to time. It is better to add the carbon disulfide by conducting a current of coal gas (from the laboratory gas supply) through a little carbon disulfide in a wash flask and thence into the solution of barium sulfide. The barium salt precipitates as a yellow crystalline powder. The filtered precipitate should be washed first with water, then with half alcohol, finally with pure alcohol and dried on a hot plate. A second crop of crystals may be obtained by allowing the wash alcohol to drain into the mother liquor.

References: Mellor, VI, 127; Friend, III (I), 255; Yeoman, *J. Chem. Soc.*, **119**, 48 (1921).

EXERCISE 77. AMMONIUM CUPROUS TRITHIOCARBONATE, $(NH_4)CuCS_3$

Dissolve 20 g. of cuprous chloride, CuCl, in the least possible volume of concentrated hydrochloric acid. Cool the solution in ice and slowly add 500 cc. of concentrated ammonia. Keeping the temperature at 0°, add 55 g. of carbon disulfide and shake vigorously at frequent intervals. After standing some 6 days in an ice box at approximately 0°, shining green crystals of the thiocarbonate separate from the solution. Filter off these crystals, wash them with cold water, and quickly dry them on paper. The potassium salt can be made with slight modifications of these directions.

References: Mellor, VI, 125; Hofmann and Höchtlen, *Ber.*, **36**, 1146, 3090 (1903).

EXERCISE 78. SODIUM THIOANTIMONATE, $Na_3SbS_4 \cdot 9H_2O$ (SCHLIPPE'S SALT)

Method I.—Intimately mix 36 g. of antimony sulfide (or powdered stibnite), Sb_2S_3; 43 g. of anhydrous sodium sulfate; and 16 g. of fine charcoal in a clay crucible, which should be about half filled with the mixture. Cover with a little charcoal and heat in the furnace to quiet fusion and then for 10 min. longer. Pour out on sheet iron or on a large iron pan. Powder the cold melt and boil it half an hour with 7 g. of sulfur and 300 cc. of water. Filter, add a little sodium hydroxide, and evaporate to crystallization in a porcelain dish. Because of hydrolysis, the crystals cannot be washed with water. Collect on glass wool or on a bare Witte plate and wash with alcohol containing a little sodium hydroxide. Obtain several crops of crystals. Finally, recrystallize from water made somewhat alkaline by sodium hydroxide and dry over lime in a desiccator, having added a few drops of ammonium sulfide to the lime. Large, water-white crystals should be obtained.

References: Mellor, IX, 570; Kirchhof, *Z. anorg. allgem. Chem.*, **112,** 67 (1920).

Method II.—In a porcelain dish, place 8 g. NaOH dissolved in 250 cc. of water, 18 g. of finely powdered Sb_2S_3, and 3 g. of powdered sulfur. Heat to boiling with frequent stirring and renew the water from time to time as it evaporates. Continue the boiling until the gray color changes to yellow. Then decant the solution through a filter of asbestos fiber, treat the residue in the dish with 50 cc. of water, and boil for a time. Again filter, unite the two filtrates, and evaporate on the water bath to crystallization. Drain the crystals on a Witte plate and dry them as in method I. A second crop may be obtained from the mother liquor.

References: Liebig, *Ann.*, **7,** 13 (1833); Vanino, Handbuch der präparativen Chemie, 3d ed., Vol. I, p. 358 (1925).

2. Double Sulfides.—Many combinations of sulfides do not correspond to any well-known oxygen analogue and are best regarded as double sulfides rather than salts of thio acids. They resemble such compounds as chromite, $Cr_2O_3 \cdot FeO$ (or $Fe(CrO_2)_2$), or spinel, $Al_2O_3 \cdot MgO$ ($Mg(AlO_2)_2$), among the double oxides. Double sulfides of copper, iron, and silver are familiar minerals.

EXERCISE 79. POTASSIUM FERRISULFIDE, $K_2S \cdot Fe_2S_3$ or $K(FeS_2)$

Mix intimately 30 g. of iron powder, 180 g. of flowers of sulfur, 150 g. of potassium carbonate, and 30 g. of anhydrous sodium carbonate and melt the mixture in a clay crucible in the furnace, which will require about an hour's heating. Allow the crucible to cool very slowly in the closed furnace. Break the crucible and digest the contents in an evaporating dish with warm water, until the lumps are entirely disintegrated. Keep draining off the greenish solution and replacing by fresh water until it remains clear, and only shining needles remain behind. Wash with water and alcohol and dry on the hot plate.

References: Friend, IX (II), 136; Schneider, *J. prakt. Chem.*, **108,** 16 (1869); (2) **2,** 141 (1870); Pavel, *Ber.*, **15,** 2605 (1882).

EXERCISE 80. AMMONIUM TETRATHIO-CUPRATE, $NH_4(CuS_4)$

Place 200 cc. of concentrated ammonia (25 per cent) and 50 cc. of water in a flask and conduct in hydrogen sulfide to saturation (closed flask). Divide the solution into two equal portions. Saturate the one with sulfur (60 g.) at 40°, filter, and add to the other half. Prepare a solution of 20 g. of crystallized copper sulfate in 200 cc. of water and add slowly and with constant shaking to the first solution until a permanent precipitate results (CuS). Filter as rapidly as possible through a large folded filter and bring the filtrate into an Erlenmeyer flask which is of a size to be nearly filled by the solution. By allowing the solution to stand, especially if cooled by ice, reddish crystals separate which should be filtered off the next day, washed with a little water and with alcohol, and dried over lime in a desiccator. To the mother liquor more copper sulfate can be added, and the process repeated.

References: Mellor, III, 228; Hofmann and Höchtlen, *Ber.*, **36,** 3090 (1903); Biltz and Herms, *Ber.*, **40,** 974 (1907).

3. Salts of Thionic Acids.—A third class of thio salts are those derived from the various thionic acids of which sodium thiosulfate and barium dithionate may be taken as examples, although the thiosulfates may also be regarded as sulfates in which one atom alone of oxygen has been replaced by sulfur (thio acid).

References: Any good text on inorganic chemistry.

EXERCISE 81. SODIUM THIOSULFATE, $Na_2S_2O_3{\cdot}5H_2O$

Prepare a solution of 126 g. of crystallized sodium sulfite, $Na_2SO_3{\cdot}7H_2O$, in 250 cc. of water, add 16 g. of finely powdered sulfur, and boil in a flask for about 2 hr. The sulfur should be almost all dissolved. Filter the solution and allow it to crystallize. The solution is easily supersaturated. Obtain a second crop from the mother liquor.

References: Bassett and Durrant, *J. Chem. Soc.*, **1927**, 1401; Young and Burke, *J. Am. Chem. Soc.*, **26**, 1413 (1904).

EXERCISE 82. BARIUM DITHIONATE, $BaS_2O_6{\cdot}2H_2O$

The preparation of this salt depends upon the preparation of manganese dithionate according to the equation

$$MnO_2 + 2SO_2 \rightarrow MnS_2O_6.$$

The more finely divided the manganese dioxide the more rapid will be the reaction, so that the precipitated reagent is better than finely powdered pyrolusite. It is still better to prepare the precipitated hydroxide $Mn(OH)_4$, by reducing the necessary quantity of potassium permanganate in neutral solution with alcohol and washing the precipitate from soluble potassium salts by decantation.

Saturate about 250 cc. of water with sulfur dioxide. The dioxide is most conveniently prepared by placing 150 g. of sodium sulfite in a flask, adding enough water to cover it, and slowly dropping into the flask through a separatory funnel concentrated sulfuric acid. Cool the solution of the dioxide by immersing it in cold water and slowly add, in small portions at a time, a suspension of about 50 g. of manganese dioxide (or the equivalent of the tetrahydroxide). Shake or stir the solution frequently and allow each portion to dissolve before adding a fresh portion. Take care to keep the temperature from rising during the addition of the dioxide. The reaction is accompanied by a side reaction according to the equation

$$MnO_2 + SO_2 \rightarrow MnSO_4.$$

This reaction is favored by high temperatures. Does this equation suggest why the manganese dioxide is added to the sulfur dioxide rather than the reverse?

When all of the manganese dioxide has been dissolved, dilute the solution to about 1.5 l., heat to boiling, and add about 200 g. of crystallized barium hydroxide in portions, testing to see when all of the manganese has been precipitated as hydroxide. (Test samples of the filtered solution with ammonium sulfide.) When a test shows that all of the manganese has been precipitated, filter roughly through cloth and then more carefully through paper; or allow the precipitate to settle in a tall jar and decant off the clear solution, repeating the operation several times and combining the decanted liquids.

Pass carbon dioxide through the filtrate until all excess of barium hydroxide has been precipitated as carbonate; filter; and evaporate to crystallization. Other dithionates can be prepared from the barium salt by double decomposition with sulfates of other metals.

References: Friend, III (I), 228; Mellor, X, 589; Marino, *Z. anorg. Chem.*, **56**, 233 (1907–1908).

Additional Exercise: Sodium tetrathionate, $Na_2S_4O_6 \cdot 2H_2O$.

XII. CHLORIDES OF THE OXYGEN ACIDS

To every oxygen acid there corresponds theoretically a chloride derived from the acid by the replacement of the hydroxyl groups by chlorine. These oxychlorides are usually liquids of rather low boiling point and high refractive index. As a rule, they react readily with water, forming free acid and hydrogen chloride. They are usually made (1) by the action of PCl_5 or PCl_3 on the anhydrous acid or its sodium salt, especially in the case of the organic acids; (2) by the direct union of an oxide with chlorine, as with $CO + Cl_2 \rightarrow COCl_2$; or (3) by the hydrolysis of the normal chloride, as $SbCl_3 + H_2O \rightarrow SbOCl + 2HCl$; $PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$.

EXERCISE 83. SULFURYL CHLORIDE, SO_2Cl_2

The plan is to conduct SO_2 and Cl_2 simultaneously into the presence of camphor, which acts catalytically to produce union. Select a large test tube (about 2.5 cm. in diameter) and fit it with a three-holed stopper. Provide two delivery tubes long enough to reach to the bottom of the test tube and a short delivery tube to be connected with a condenser. Place 50 g. of camphor in the test tube and enough glass beads (or bits of broken tubing) to two-thirds fill the tube. Insert the stopper carrying three tubes. The delivery tube is connected with a condenser which in turn is connected with the neck of a second distilling tube of 200 cc. to act as a receiver, the exit tube of which leads to the draught in the hood. At the outset, the test tube containing the camphor is cooled with a bath of ice water, which is later removed as the reaction becomes moderated. Dry SO_2 is first conducted into the camphor until it melts to a clear fluid, and then dry chlorine is led in at the same rate. The SO_2 is prepared by gently treating 400 g. of copper turnings or foil with 800 g. of concentrated sulfuric acid, the mixture being contained in a round-bottomed flask and heated on a sand bath. The flask should have a thistle tube, and the SO_2 should be bubbled through a wash flask of concentrated H_2SO_4. The chlorine is prepared in a similar flask from 500 g. of coarsely powdered MnO_2 and 500 cc. of concentrated HCl and is also dried by H_2SO_4. The rate of flow of the two gases is regulated by the flame and can be watched by the rate at which bubbles flow in the wash flasks. An excess of chlorine is indicated by the yellow color of the liquid in the test tube containing the camphor. The gases are conducted in until the test tube is half full of the liquid. Toward the end, see that the chlorine is in decided excess and then decrease it by increasing the SO_2.

After some hours' standing—best until the next morning—the test tube is heated on a water bath, and the liquid is distilled off. If the distillate contains free chlorine, a little mercury is added and shaken with the liquid, which is then redistilled after filtration through a dry asbestos mat on a Witte plate. The final distillation should take place from a flask furnished with a thermometer, and the liquid should boil at 69.5°. It should be preserved in a sealed tube. The camphor may be used indefinitely, as it takes part in a cycle of reactions and is left at the end of the reaction in very nearly its original state.

References: Mellor, X, 666; Friend, VII (II), 91; Schulze, *J. prakt. Chem.*, (2) **24,** 168 (1881); Durrans, *J. Soc. Chem. Ind.*, **45,** 347 (1926).

Sulfuryl Chloride—Alternate Method.—Set up the apparatus represented in Fig. 22. *A* is a large test tube

5 to 6 cm. in diameter and about 14 cm. in height. About 3 cm. from the top, seal in the overflow tube *E*, which slopes gently downward at first, then becomes vertical, passing through the stopper in cylinder *C*. It must be wide enough to permit liquid to flow from *A* to *C* while allowing displaced gases to pass in the opposite direction. Through the rubber stopper to *A*, pass the rather wide tube *F* through which the mixed gases are brought into contact with activated charcoal in *A*. *G* is a tube for the escape of unabsorbed gases, leading to an absorbent solution of sodium hydroxide. *B* is a mixing flask for the two gases and a safety valve in case of back pressure. *D* is a large beaker containing crushed ice and salt.

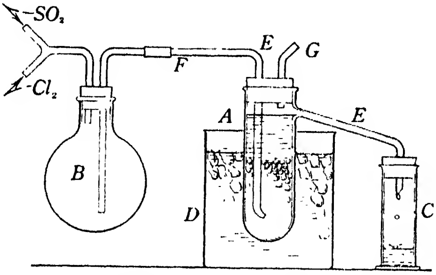


FIG. 22. Preparation of sulfuryl chloride.

Fill *A* with well-activated charcoal to within 1 to 2 cm. of the overflow tube *E*. Immerse *A* in *D* and conduct in the two gases sulfur dioxide and chlorine, in equal volumes, best from cylinders of compressed gas. Action begins at once with considerable heat evolution, and after a time the union of the gases becomes almost quantitative. The flow of the two gases should be regulated so that the least number of bubbles escapes through the liquid collecting in *A*. Temperature is of great importance. The colder the better, so an ice-salt mixture is very necessary for a large yield.

References: Danneel, *Z. angew. Chem.*, **39,** 1553 (1926); McKee and Salls, *Ind. Eng. Chem.*, **16,** 279, 351, 833 (1924).

EXERCISE 84. CHROMYL CHLORIDE, CrO_2Cl_2

Fuse 50 g. of sodium chloride with 60 g. of potassium dichromate in a furnace; then cool and powder the product finely. Place the powder in a distilling flask provided with a dropping funnel, the bulb of which contains concentrated sulfuric acid. Connect a condenser with the distilling flask and provide a flask as a receiver, arranged so as to be immersed in an ice bath. Slowly drop in the sulfuric acid, adding enough completely to decompose the salts present and to provide an excess sufficient to hold back the water generated in the reaction. When sufficient acid has been added, heat the flask and distill over the dark-red chromyl chloride. Provide a clean and dry distilling flask and redistill the product, the boiling point of which is given as 118°. Some slight decomposition may take place in distilling under atmospheric pressure, so that the boiling point tends to be a little low. A slow current of dry air passed through the liquid will tend to stabilize it. Preserve in a sealed tube.

References: Friend, VII (III), 28; Mellor, XI, 391; Wöhler, *Pogg. Ann.*, **33,** 343 (1834); Moler and Gómez, *Z. phys. Chem.*, **80,** 513 (1912).

Additional Exercises: $SOCl_2$; $POCl_3$; $PSCl_3$.

XIII. ALUMINOTHERMIC REDUCTION

Although a great deal of heat is set free when hydrogen burns in oxygen (69 Cal.) or when carbon burns (94.4 Cal.), the temperature that can be realized is not so very high. Above a certain point, the products of combustion begin to dissociate and in so doing absorb heat, and this sets a limit to the temperature that can be realized. In the combustion of many of the metals, an even greater amount of heat is evolved, and the oxides formed are stable beyond 3000°. Consequently, combustion of this kind will produce an extremely high temperature. The following table from International Critical Tables gives the heat of formation of the oxides of a number of the metals:

HEAT OF FORMATION OF SOME OXIDES

	Calories		Calories
CaO	151.7	CO_2	94.4
MgO	146.	SiO_2	201.3
La_2O_3	456.9	TiO_2	217.4
Cr_2O_3	267.4	ThO_2	331.
Al_2O_3	389.5	MoO_2	131.4
Fe_2O_3	190.7	WO_3	191.4

Since aluminum is now a cheap material, advantage is taken of its high heat of combustion and stable oxide to produce high temperatures in considerable masses of materials in the process of welding broken rails, shafts, and castings. Powdered aluminum and a reducible oxide are packed around the fracture in a sand mold, and the charge is ignited. A liquid slag of aluminum oxide results, and the heat of the reaction fuses the broken pieces of metal together (thermite welding). Many incendiary bombs were composed of aluminum powder and a metallic oxide.

Since the heat of combustion of aluminum is greater than that of almost any other common metal, it follows that at a high temperature aluminum will reduce almost any metal from its oxide, and in many cases this affords an easy method of preparing difficultly reducible metals (Goldschmidt method of reduction).

In some cases, as with vanadium or thorium, the excess of aluminum alloys with the reduced metal. In these cases, the aluminum may be replaced by the so-called *mischmetal.* This is an alloy obtained by the reduction of the mixed oxides of the rare earths.

References: Mellor, V, 217; Goldschmidt, *Ann.*, **301,** 19 (1898); *J. Soc., Chem. Ind.*. **17,** 543 (1898); *Z. Elektrochem.*, **4,** 494 (1898).

EXERCISE 85. METALLIC MANGANESE, Mn

Place 100 g. of finely powdered pyrolusite, MnO_2, in a Hessian crucible and heat it in a gas furnace to convert it into Mn_3O_4 (the reaction with MnO_2 is too violent). Weigh the Mn_3O_4 thus obtained and mix it with a little less than the weight of granulated aluminum required for its reduction:

$$3Mn_3O_4 + 8Al \rightarrow 4Al_2O_3 + 9Mn.$$

Do not use the fine powder employed in making silver paints. Place three or four spoonfuls of the mixture in a Hessian crucible, which will easily contain all of the mixture. Make a little depression in the mixture in the crucible and in this place a "starting mixture" of 1 g. of aluminum and 10 g. BaO_2 (thoroughly mixed). Insert one end of a piece of magnesium ribbon in the mixture (as a fuse). Set the crucible deep in sand on a sand bath in a location where flying sparks will cause no harm. Set fire to the magnesium ribbon with a Bunsen flame and, after the reaction is well started, rapidly ladle in the remainder of the mixture with a metal spoon, protecting the hand with a glove and the eyes with dark goggles. When the reaction is over and the crucible has cooled, break the latter. A solid slag of aluminum oxide (corundum) will be found, hard enough to scratch glass. If the operation has been successful, the manganese will form an ingot under the slag; if the reaction has been a little slow, the manganese will form pellets embedded in the slag.

References: Friend, VIII, 259; Mellor, XII, 164; Goldschmidt, *Z. Elektrochem.*, **4,** 497 (1898).

EXERCISE 86. CHROMIUM, Cr

The reduction between aluminum and chromium sesquioxide proceeds with much less heat evolution than with manganese oxide, and with small quantities of material the heat is sometimes insufficient to melt the slag of aluminum oxide. The addition of a little dichromate increases the heat and gives better results. For the charge, mix 70 g. of Cr_2O_3 with about 1 g. less than the theoretical weight of aluminum. Place all of the mixture in the Hessian crucible, which should be about three-fourths full. Ignite as before with a starting mixture and magnesium fuse. Rubies may sometimes be found in the slag.

References: Friend, VII (III), 9; Mellor, XI, 134; Goldschmidt, *Z. Elektrochem.*, **4,** 494 (1898); *J. Soc. Chem. Ind.*, **17,** 543 (1898).

EXERCISE 87. SILICON, Si

Mix 100 g. of granulated aluminum with 90 g. of clean fine sand and 90 g. of sulfur. Place the mixture in a fire-clay crucible embedded in sand in a safe place and ignite with fuse powder and a magnesium ribbon, as described in Exercise 85. After the reaction is completed, allow the crucible to cool. Break the crucible, put the contents in an evaporating dish, and treat with water to decompose the aluminum sulfide. This should be done under the hood so that the copious fumes of *poisonous* H_2S will be carried off. Wash away the slimy lumps of melted aluminum from such foreign matter as pieces of crucible. Place these pieces of metal in a beaker, gradually treat with commercial hydrochloric acid until the action has quieted down, then cover with the acid and let stand on the hot plate for several days, replenishing the acid whenever necessary. Pour off the liquid and boil the crystal powder with pure concentrated acid. Again decant, place the crystals in a platinum dish, treat with hydrochloric acid a little at a time, and then leave on the water bath for about an hour. This treatment should remove any undecomposed sand or particles of crucible. Dilute the acid and pour it off, wash the crystals well by decantation with water, and collect on an ordinary filter or on a Büchner funnel. Finally, dry the crystals on the hot plate.

References: Mellor, VI, 149; Friend, V, 179; use of sulfur, Kühne, *Chem. Zentr.*, **1904,** I, 64.

XIV. ELECTROCHEMICAL REPLACEMENT

Among the metals, it is a well-recognized principle that a metal high in the electrochemical series will displace one lower in the series from its salts. This principle is sometimes employed in separating silver from its salts:

$$Cu + Ag_2SO_4 \rightarrow CuSO_4 + 2Ag.$$

Similarly with the nonmetals, chlorine displaces iodine:

$$2KI + Cl_2 \rightarrow 2KCl + I_2.$$

On the other hand, from oxygen compounds, iodine will displace chlorine:

$$2KClO_3 + I_2 \rightarrow 2KIO_3 + Cl_2.$$

In a similar way, oxygen displaces sulfur from many compounds on long-continued exposure to air.

EXERCISE 88. PREPARATION OF POTASSIUM IODATE FROM POTASSIUM CHLORATE

In a suitable flask (200 cc.), dissolve 25 g. of potassium chlorate in 50 cc. of water and to this add 27 g. of iodine.

Warm the mixture to 60 to 70° and add 1 to 2 cc. of concentrated hydrochloric acid (under a good hood). After a short time, a vigorous evolution of chlorine takes place, together with some vaporization of iodine and iodine chloride. Some of the iodine may be saved and washed back into the reaction mixture by placing a small empty funnel in the neck of the flask.

When the reaction ceases, heat the solution to drive out the chlorine, then add a little iodine to replace any loss (1 g.). Heat once more and then allow the solution to cool. Most of the iodate crystallizes and should be filtered off. A second crop may be obtained from the mother liquor.

The united crystals usually contain some acid iodate. They should be dissolved in a small volume of water (100 cc.), carefully neutralized with dilute potassium hydroxide, and recrystallized.

References: Friend, VIII, 243; Mellor, II, 332; Schlötter, *Z. anorg. Chem.*, **45,** 270 (1905).

XV. TRANSITION POINTS IN SALTS

A great many solids are capable of existing in two or more crystalline forms, the form obtained in any given case depending upon the temperature. Above a certain temperature (called the *transition temperature*), one form is stable, while below the transition temperature a different form is obtained. Sometimes the change from one form into the other is reversible, so that by alternately heating and cooling the solid past the transition temperature the two forms can be changed each into the other as often as may be desired. The compound is then said to be *enantiotropic*. In other cases, the change takes place in one direction only and cannot be directly reversed by reversing the temperature (*monotropic*).

Ammonium nitrate exists in four different forms, all of which are enantiotropic; the change of white phosphorus into the red (or violet) variety is monotropic. Mercuric iodide exhibits a striking example of an enantiotropic transition. Above 126.3°, it is obtained in yellow rhombic crystals; while below that temperature, a scarlet tetragonal modification appears.

In crystallizing salts from solution, it frequently happens that it is possible to obtain more than one hydrate. In all such cases, a perfectly definite temperature can be found above which the one hydrate will deposit, and below which the other one with a larger number of molecules of water of hydration appears. Thus, above 38°, zinc sulfate deposits crystals of the composition $ZnSO_4 \cdot 6H_2O$, while crystals deposited below that temperature have the formula $ZnSO_4 \cdot 7H_2O$. This is also called a transition point.

Hydrates are merely one form of a double salt, and it often happens that other double salts as well as hydrates exhibit transition or decomposition points. Salts, whether simple or double, that have transition points at which color changes occur are of special interest. Mercuric iodide is a striking example of such a simple salt and is easily prepared by double decomposition. The preparation of a few other examples will be described.

References on Transition Points: Textbooks on physical chemistry; Findlay, The Phase Rule, 32, 227, 279, 6th ed. (1927); Friend, I, 67; Mellor, I, 52.

EXERCISE 89. CUPROUS IODOMERCURATE, $Cu_2(HgI_4)$

Prepare a solution of 6.8 g. of mercuric chloride in about 50 cc. of water and a second solution of 18.3 g. of potassium iodide in 100 cc. of water; divide the latter solution into two equal portions and slowly add one of these to the solution of mercuric chloride. Wash the resulting precipitate once by decantation and then dissolve it in the second portion of the solution of potassium iodide. The mercuric iodide dissolves in consequence of the formation of a soluble complex salt having the formula $K_2(HgI_4)$. The insoluble cuprous iodomercurate is prepared from this by precipitation. To the solution add a concentrated solution containing 12 g. of copper sulfate. Reduce the copper to the cuprous state by conducting into the solution a current of sulfur dioxide. A bright red precipitate forms having the composition $Cu_2(HgI_4)$. When the precipitation is complete, collect the material on a filter, pump as dry as possible, and spread it in a warm place to complete the drying.

At about 71°, the red salt changes color to black rather sharply, and this change is reversible within a narrow limit of temperature.

$$Cu_2(HgI_4) \rightleftharpoons 2CuI + HgI_2.$$

This change is best observed by sealing a small quantity of the compound in a thin-walled glass tube and slowly heating it in a water bath, using a thermometer as a stirring rod.

References: Mellor, IV, 935; Meusel, *Ber.*, **3**, 123 (1870); Duboin, *Ann. chim. phys.*, (8) **16**, 258 (1909).

EXERCISE 90. SILVER IODOMERCURATE, $Ag_2(HgI_4)$

As in the last exercise, prepare a solution containing about 5 g. of dissolved potassium iodomercurate in about 50 cc. of water. To this add a dilute solution of silver nitrate as long as precipitation continues.

The transition point of the silver iodomercurate is not so sharp as that of the corresponding cuprous salt. The transition takes place between 40 and 50°, the salt being yellow below the transition point and red above it. A sample should be sealed in a thin-walled glass tube and preserved as a permanent specimen.

References: Mellor, IV, 937; Meusel, *Ber.*, **3**, 123 (1870); Wegelius and Kelpi, *Z. anorg. Chem.*, **61**, 415 (1909).

EXERCISE 91. POTASSIUM CUPRIC CHLORIDE, $2KCl{\cdot}CuCl_2{\cdot}2H_2O$

This double salt is made easily by dissolving potassium chloride, KCl, and cupric chloride, $CuCl_2{\cdot}2H_2O$, in water in the proportion of two molecules of the former to one of the latter and evaporating the solution to crystallization. This salt, as well as the corresponding ammonium salt, is used in the determination of carbon in iron. Iron dissolves in a concentrated solution of the salt, leaving the carbon undissolved, and the latter can be filtered off and estimated by combustion.

At a temperature of about 92°, the blue, plate-shaped crystals change into a brownish-colored mass in which can be distinguished the white octahedra of potassium chloride. The decomposition may be expressed in the equation

$$2KCl{\cdot}CuCl_2{\cdot}2H_2O \rightleftharpoons KCl{\cdot}CuCl_2 + KCl + 2H_2O.$$

The change is enantiotropic, but the reverse transformation is much slower than the direct decomposition.

Obtain the salt in small crystals and carefully dry them. Seal a small sample in a thin-walled glass tube and determine the transition point by using the tube as a stirring rod in a beaker of water that is being heated. When approaching the transition point, regulate the flame so as to raise the temperature of the water very slowly.

References: Friend, II, 274; Mellor, III, 188; Metscherlich, *J. prakt. Chem.*, (1) **19,** 449 (1840); Meyerhoffer, *Z. phys. Chem.*, **5,** 98 (1890).

EXERCISE 92. CALCIUM CUPRIC ACETATE, $Ca(C_2H_3O_2)_2 \cdot Cu(C_2H_3O_2)_2 \cdot 6H_2O$

The double acetate is prepared in the same general way as the double chloride but by dissolving one molecule of copper acetate with three molecules of calcium acetate.

It exhibits a transition point at 76 to 78°. The blue double salt becomes moist in spots and changes into a green copper salt interspersed with needles of white calcium acetate.

Reference: Rüdorff, *Ber.*, **21,** 279 (1888).

XVI. METALLO-ORGANIC COMPOUNDS (GRIGNARD'S SYNTHESIS)

A great many compounds have been prepared consisting of some metal or metalloid combined with various organic radicals. Some of these, as zinc ethyl and tin ethyl, have played an important part in chemical history (Frankland's work on valence); some constitute important pharmaceutical preparations; some are well-known chemical reagents (Grignard's reagent); many have been investigated as antiknock materials in gasoline. An example will illustrate the general method of preparation.

Reference: Friend, XI (I).

EXERCISE 93. LEAD TETRAPHENYL, $Pb(C_6H_5)_4$

To 70 g. of ether, thoroughly dried over metallic sodium, add 25 g. of brombenzene and 3.7 g. of magnesium ribbon that has been rubbed bright with fine sandpaper. Close the flask with a calcium chloride tube and allow it to stand 24 hr. in an evaporating dish containing water, to prevent undue rise in temperature:

$$C_6H_5Br + Mg \rightarrow C_6H_5MgBr.$$

When the magnesium has disappeared, add 24 g. of dry, carefully powdered lead chloride in small quantities at a time and with frequent shaking. Allow the mixture to stand two days with occasional shaking.

In small portions at a time, add 200 cc. of water, faintly acidulated with hydrochloric acid. Collect the dark precipitate on a Büchner funnel and dry it thoroughly. Place the dark solid in a flask with a reflux condenser and boil with 100 cc. of benzene. Filter off the benzene through a folded filter, leaving the solid in the flask. Repeat the extraction with benzene several times. Combine the filtrates and concentrate to a volume of about 75 cc. On cooling, lead tetraphenyl separates from the solution in colorless needles which melt at 222°:

$$2PbCl_2 + 4C_6H_5MgBr \rightarrow$$
$$Pb + Pb(C_6H_5)_4 + 2MgCl_2 + 2MgBr_2.$$

References: Friend, XI (I), 339; Pfeiffer and Truskier, *Ber.*, **37,** 1126 (1904); Gilman and Robinson, *J. Am. Chem. Soc.*, **49,** 2315 (1927).

Additional Exercises: Tin tetraphenyl, $Sn(C_6H_5)_4$, Friend, XI (I), 316; Pfeiffer and Truskier, *Ber.*, **37,** 319 (1904); Chambers and Scherer, *J. Am. Chem. Soc.*, **48,** 1054 (1926); Mercury diphenyl, $Hg(C_6H_5)_2$, Friend, X (I), 72; Maynard, *J. Am. Chem. Soc.*, **46,** 1510 (1924).

PART III

THE COLLOIDAL STATE OF MATTER

When any sparingly soluble material is coarsely powdered and then shaken with a solvent and set aside, the powder quickly settles to the bottom of the vessel. The more finely the material is powdered the slower is the process of settling and the more imperfect becomes the process of separation by filtration. It is conceivable that the process of powdering should be so perfect as to separate the material into its ultimate molecules, and when the solute is then shaken with the solvent, the dispersion of the one through the other would be the same as in a true solution. All gradations between coarse suspensions and complete molecular mixing are sometimes designated as *dispersed systems*, and it is clear that any possible degree of dispersion between these limits may occur. The more imperfect dispersed systems are *suspensions*. These are turbid in appearance, settle more or less completely in time, and are more or less perfectly filterable. At the other end of the series are the true solutions. These do not settle, are not filterable, and are perfectly translucent. When a beam of light is passed through a true solution, there is no dispersion of light by reflection from suspended particles, and the path of the beam through the solution is not visible. The solution is said to be *optically void*.

Intermediate between undoubted suspensions and undoubted solutions is a class of dispersed systems called *colloids*. A beam of light passed through a colloid leaves a bright path (*Tyndall cone,* Fig. 23) owing to reflections from suspended particles, just as a beam of sunlight in a dark room is luminous because of the reflection from dancing dust particles, and the light so scattered is polarized. Yet the particles of the colloid are too small to make the system turbid in appearance (though it may be strongly colored), and they cannot be removed by ordinary filters. These particles are restrained by membranes of parchment or animal tissues, while materials in true solution pass through these; so the colloid may be separated from truly dissolved substances by allowing the latter to diffuse away through such membranes (dialysis). The particles of a colloid do not settle, for they are subject to the same kinetic movements as prevail among dissolved molecules and maintain a constant motion (Brownian movements). There is no natural and sharp distinction between a colloid and a suspension, but if the diameter of the particles range between 1mμ and 100mμ, the system is usually classed as a colloid. (1mμ = 0.000,001 mm.)

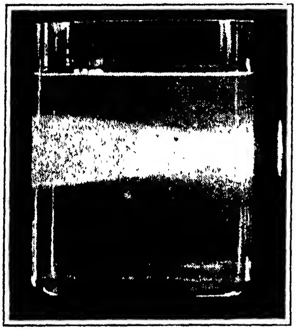


FIG. 23.—Tyndall cone.

It will be observed that a colloid is not a member of a particular class of substances but a state of matter and that any substance under the proper conditions may become a colloid, just as it may become a solid, a liquid, a gas, or a solution.

Under some conditions, a colloid thickens (increases in viscosity) until it resembles an ordinary jelly. This condition is called a *hydrogel* or, more briefly, a *gel;* to distinguish it from the hydrogel, the ordinary state of the colloid is often called the *hydrosol* or the *sol.* Sometimes the hydrogel is converted into the hydrosol by the action of some reagent. The reagent is then called a peptizing reagent, and the process is referred to as the *peptizing* of the gel.

References: Friend, I, 78; Mellor, I, 768; Alexander, Colloid Chemistry, 4 vols. (1926–1932); Bancroft, Applied Colloid Chemistry (1926); Bogue, Colloidal Behavior, 2 vols. (1924); Colloid Symposium Monographs, beginning 1923; Hatschek, Introduction to the Physics and Chemistry of Colloids (1922); Thomas, Colloid Chemistry (1934); Weiser, The Colloidal Salts, (1928); The Hydrous Oxides (1926); Inorganic Colloid Chemistry (1933).

I. MODES OF PREPARING COLLOIDS

From what has been said, it will be seen that colloids may be prepared by methods which reduce the size of larger particles to colloidal dimensions or by starting with true solutions and bringing about the first step toward crystallization or precipitation. The methods employed are sometimes grouped in three classes:

1. Crystallization methods: starting with a solution and producing a colloid.
2. Solution methods: starting with a suspension and producing a colloid (peptization).
3. Electrical dispersion: sparking between electrodes under a solvent whereby the particles of the electrodes are torn off in colloidal dimensions.

1. Crystallization Methods.—This name is employed because it has been thought that the formation of a colloid is the first step in crystallization.

1. *By Change in the Solvent.*—A solute, soluble in one solvent but not in a second, is selected. A dilute solution in the one solvent is prepared, and the solution is poured slowly and with constant stirring into the second solvent, occasioning a colloidal dispersion.

EXAMPLE 1. A dilute solution of gum mastic in alcohol is poured slowly into a large volume of water. A saturated solution of sulfur in alcohol is poured into water.

EXAMPLE 2. A somewhat different method is illustrated by dissolving a little silver iodide in a solution of potassium iodide, the latter solution being considered as the solvent. This solution is then poured into a large excess of pure water which breaks up the complex iodide and produces colloidal silver iodide.

2. *By Processes of Reduction.*—Many insoluble bodies are formed by chemical reduction and under the proper conditions may be produced in the colloidal state.

EXERCISE 94. PURPLE OF CASSIUS

Add a few drops of a solution of gold chloride (6 g. $HAuCl_4 \cdot 3H_2O$ per liter) to about 5 cc. of water. To 50 cc. of water add one or two drops of a dilute solution of stannous chloride and one or two drops of a solution of sodium hydroxide. Add a little of this solution drop by drop, with constant stirring, to the solution of gold chloride. A deep rose-purple color, known as the purple of Cassius, slowly develops. It is due to finely divided gold.

References: Friend, II, 330; Mellor, III, 564; Weiser, The Hydrous Oxides, p. 218 (1926); Inorganic Colloid Chemistry, vol. I, Chaps. II, III (1933); Müller, *J. prakt. Chem.*, (2) **30,** 252 (1884); Schneider, *Z. anorg. Chem.*, **5,** 80 (1894).

EXERCISE 95. RED GOLD SOL (METHOD OF ZSIGMONDY)

Place about 120 cc. of pure water in a Pyrex beaker of 300 to 500 cc. capacity and heat to boiling. While warming the water, add 2.5 cc. of a solution of gold chloride (6 g. crystallized $HAuCl_4 \cdot 3H_2O$ per liter) and 3 cc. of a solution of pure potassium carbonate (0.2

normal). As soon as the solution boils, add 3 to 5 cc. of a solution of formaldehyde (0.3 cc. commercial formalin in 100 cc. of water) rather rapidly and with constant stirring. (A soft-glass rod must not be used. Use a piece of hard-glass tubing.) The solution should assume a bright red color. The colloidal gold may be purified by dialysis from the soluble materials present.

References: Friend, II, 329; Mellor, III, 554; Zsigmondy, *Ann.*, **301,** 29 (1898); Nicol, *J. Soc. Chem. Ind.*, **46,** 179 (1927); **47,** 343 (1928).

Alternate Method.—Unless the greatest care is exercised to secure perfectly pure reagents, including water, the gold colloid instead of red will be purple, a color which indicates a coarser state of aggregation. Red gold may be obtained with much greater ease by proceeding as follows: In an Erlenmeyer flask put 100 cc. of distilled water and add a few drops of a neutralized 1 per cent solution of gold chloride. After shaking, add a few drops of a very dilute solution of tannin (about 0.1 per cent). Heat to boiling over a Bunsen flame. When the red color begins to form, add alternate portions of the two reagents until a deep red tint is secured. The tannin acts as a reducing agent. It also acts as a *protecting* colloid. Many materials can be obtained and preserved in colloid form in the presence of an added colloid called a protecting colloid.

Reference: Ostwald-Fischer, Theoretical and Applied Colloid Chemistry, p. 23 (1922).

EXERCISE 96. COLLOIDAL SILVER

Prepare a very little silver oxide by treating a dilute solution of silver nitrate with sodium hydroxide and washing a number of times by decantation. Shake the oxide vigorously with about 200 cc. of water and finally filter the solution. Place it in a flask, heat to 60°, and conduct into the solution a rapid current of pure hydrogen gas. In about half an hour, a yellow colloidal solution of silver is produced.

References: Mellor, III, 554; Friend, II, 294; Kohlschütter, *Z. Elektrochem.*, **14**, 49 (1908); Garard and Duckers, *J. Am. Chem. Soc.*, **47**, 692 (1925).

3. *By Processes of Double Decomposition.*—Many instances of double decomposition can be so arranged as to produce a colloidal dispersion instead of precipitation.

EXERCISE 97. COLLOIDAL ANTIMONY SULFIDE

A solution of H_2S gas is made by saturating 200 cc. of distilled water in a 500-cc. flask with H_2S gas. Two hundred cubic centimeters of a 1 per cent solution of tartar emetic (potassium antimonyl tartrate, $K(SbO)C_4H_4O_2 \cdot \frac{1}{2}H_2O$) is slowly run into the H_2S solution through a dropping funnel, while at the same time a moderate stream of H_2S gas is passed into the solution. The orange-red colloidal suspension thus formed is freed of H_2S by passing hydrogen through it until the smell of H_2S can no longer be detected. The foreign salts remaining from the double decomposition must next be removed. This is accomplished by dialysis. The solution is placed in a previously wetted parchment tube of about 3 cm. in diameter and about 60 cm. in length which is bent in a U shape and immersed in a tall, wide cylinder of distilled water. The ends of the tube are tied with string, but, since they project above the water, the tying need not be very tight. After immersion in the water, the parchment should be immediately inspected for holes, through which the red solution will stream out into the clear water. A hole may be "tied out" by tying one piece of stout string *tightly* above and another below the leak, thus making two or more sections, or "sausages."

References: Mellor, IX, 526; Weiser, The Colloidal Salts, p. 58 (1928); Schulze, *J. prakt. Chem.*, (2) **27,** 320 (1883); Biltz, *Ber.*, **37,** 1097 (1904).

Additional Exercises: HgS from $Hg(CN)_2$ or $Hg(C_2H_3O_2)_2$; As_2S_3, *J. Am. Chem. Soc.*, **37,** 2024 (1915).

EXERCISE 98. COLLOIDAL FERRIC HYDROXIDE, $Fe(OH)_3$

Dissolve about 10 g. of crystallized ferric nitrate in 200 cc. of water to which 2 cc. of nitric acid has been added and heat the solution to boiling. A part of the ferric nitrate undergoes hydrolysis, as is indicated by the deepening of the color of the solution. If the solution is now cooled the color becomes lighter owing to the reversing of the reaction of hydrolysis. While the solution is nearly boiling, add metallic copper (best in the form of fine powder) in small portions at a time. The free nitric acid acts upon the copper and is removed from the field of action. In accordance with the law of mass action, the hydrolysis will now move to completion. When no further action is observed, dilute the solution to about 300 cc. and filter rapidly. The colloidal ferric hydroxide is very deep red in color and by transmitted light is perfectly clear. By reflected light it looks muddy. Boil a small portion in a test tube for a time. No coagulation is observed. To another portion in a test tube add one drop of concentrated sulfuric acid and again boil. The ferric hydroxide is coagulated and can be entirely removed by filtration. (The filtrate will be colored by the copper salts present.) The copper salts, being soluble, can be removed by dialysis, leaving a very stable sol of ferric hydroxide which will keep indefinitely. A much more rapid method consists in heating a large volume of water (500 cc.) to boiling and adding, a drop at a time, 5 cc. of a 33 per cent solution of ferric chloride. The salt is hydrolyzed by the hot water.

Compare the color of the sol with that of a solution of ferric chloride to which an excess of sodium acetate has been added. How does this solution behave when boiled?

References: Friend, IX (II), 125; Mellor, XIII, 831; Cohen, *J. Am. Chem. Soc.*, **36,** 19 (1914); Powis, *J. Chem. Soc.*, **107,** 818 (1915); Weiser, The Hydrous Oxides, p. 38 (1926).

2. Solution Methods.—The following will serve as an example of the process of bringing a precipitate into colloidal form.

EXERCISE 99. COLLOIDAL CADMIUM SULFIDE, CdS

Dissolve 5 g. of cadmium sulfate in water, add about 5 cc. of ammonia, and precipitate the cadmium sulfide by a current of hydrogen sulfide. Wash the precipitate with pure water repeatedly (by decantation). Suspend it in pure water and conduct into the suspension a rapid current of hydrogen sulfide. The precipitate at first assumes a milky appearance and finally disappears. Boil the sol until the excess of hydrogen sulfide is driven off.

References: Friend, III (II), 183; Mellor, IV, 606; Meldrum, *Chem. News*, **79,** 170 (1899); Prost, *J. Chem. Soc.*, **54,** 653 (1888); Vanino and Hartl, *Ber.*, **37,** 3622 (1904); Weiser, The Colloidal Salts, p. 93 (1928).

3. Method of Electrical Dispersion (Bredig's Method).

EXERCISE 100. COLLOIDAL PLATINUM, Pt

Colloidal platinum may be prepared very easily by arcing under distilled water between platinum electrodes (Fig. 24). The current is taken from an ordinary 110-volt lighting circuit through an ammeter and an adjustable resistance in series or simply through a known resistance. The current should be from 6 to 10 amp. If the ammeter is not used, the resistance must be high enough so that not more than 10 amp. can pass, since many lighting circuits are fused for 10 amp. The minimum permissible resistance can be calculated from Ohm's law, where $R = E/I$. Inserting the voltage and maximum allowable amperage, we have $^{110}/_{10} = 11$ ohms. Since there is such a wide range permitted in the amperage, the resistance need not be known to any great degree of exactness. The electrodes may be made of heavy wire sealed into glass tubes which serve as insulating handles. One of the electrodes is clamped so that it is well under the surface of 100 to 150 cc. of distilled water in a small beaker. The other is held in the hand, touched to the first, and quickly withdrawn a little so that an arc is formed. This is usually of very short duration and must be reformed. This process is continued until the solution is dark colored. A trace of dilute alkali may be added if the platinum does not seem to go into solution very rapidly. The coarser particles

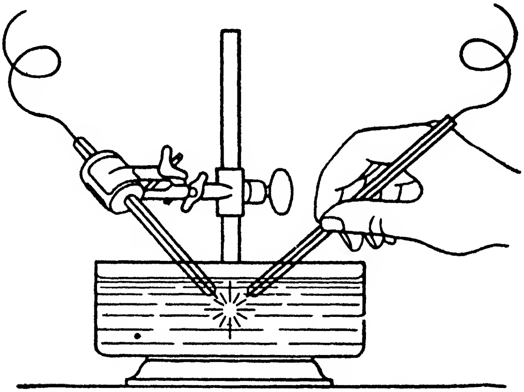


FIG. 24.

of platinum should be filtered off, and some characteristic reactions tried as follows:

1. Try the action of an electrolyte on colloids by adding a salt solution. The platinum should precipitate after a time.

2. To a solution of hydrogen peroxide, add some of the colloidal platinum solution. The catalytic action of the finely divided platinum is plainly evidenced by the evolution of oxygen.

3. The "poisoning" of a catalyst may be shown by adding some hydrogen sulfide solution to the hydrogen peroxide before the colloidal platinum is introduced. No decomposition of the peroxide is observed in this case, since the platinum has been poisoned by the presence of the hydrogen sulfide. This method is applicable to most of the metals below hydrogen in the electrochemical series.

References: Friend, IX (I), 269; Mellor, III, 557; Bredig, *Z. angew. Chem.*, **11,** 951 (1898); *Z. Elektrochem.*, **4,** 514 (1898); Beans and Eastlack, *J. Am. Chem. Soc.*, **37,** 2667 (1915); Benton, *J. Phys. Chem.*, **30,** 1415 (1926).

II. DIALYSIS TESTS FOR COLLOIDS

Many colloids are highly colored, and the question often arises as to whether the color of a given liquid is due to a small amount of a colloid or to a much larger amount of some dissolved substance; a very simple experiment in dialysis will often serve to decide the matter.

EXERCISE 101. PREPARATION OF THE DIALYZER

A suitable dialyzer may be made from collodion in the following way: Obtain a rather large test tube (2 to 2.5 cm.) and pierce a very small hole in the bottom (1 to 2 cm.), taking care that the bottom is left perfectly smooth. Prepare a solution of collodion (if none is ready at hand), by placing 3 g. of pyroxylin in a flask, adding 75 cc. of ether, and corking. After about 15 min., add 25 cc. of ethyl alcohol. The solution should be entirely clear.

Dip a cork in the collodion and daub it on the bottom of the test tube (to close the hole), repeating the process several times and allowing the collodion to dry between repetitions. Pour the collodion into an open dish and dip the tube into it so as to wet the outside of the tube to a height of about 2 in. Allow the layer of collodion to dry in the air for about 10 min. till it no longer sticks to the fingers; then plunge the tube into water and also pour water into it. By blowing gently into the tube, the sac of collodion should separate from it and be removed easily. Have ready a short piece of glass tubing of the same size as the test tube. Cement the sac to this tube with collodion. You now have a very good dialyzer supported by a glass rim.

A very serviceable dialyzer may be made from a Soxhlet cartridge by following the directions of Briggs. Select a large cartridge of rather thick paper and fill it with a collodion solution. As soon as the solution has completely impregnated the pores of the paper, pour it out and allow the cartridge to dry for a few minutes until the collodion has set. Again fill the cartridge with collodion and repeat the process until three coats have been deposited. After draining for the third time, allow the cartridges to dry until the ether has evaporated but not all of the alcohol. Then immerse in water and preserve under water for use. If the collodion becomes completely dry, it will be almost impervious to water.

The solution to be tested is placed in the collodion sac, and the latter is immersed in water. A colloid will not diffuse into the external water, while a dissolved substance will. With dialyzers prepared as described, try the diffusibility of any colloidal solutions that you may have at hand. Make dilute solutions of several dyes, as eosin, malachite green, and Congo red. Do these dialyze through the membrane?

References: Bigelow and Gemberling, *J. Am. Chem. Soc.*, **29**, 1576 (1907); Hill, *ibid.*, **27**, 1058 (1905); Holmes, *ibid.*, **38**, 1204 (1916); Briggs *J. Phys. Chem.*, **19**, 377 (1915).

III. GELS

A colloid is always to be thought of as a two-phase system, and the type that we are considering consists of a solid dispersed through a liquid. When the particles of the solid clump together into large masses, a precipitate of the gel may occur; or the aggregation may take the form of very fine films that constitute a network, or honeycomb, structure. The interstices in the system become filled with the liquid, and the whole system assumes the form of a typical jelly. Some solids do not seem ever to form a jelly, and, in the main, these are solids that have little affinity for water and show no tendency to become hydrated. An example of this sort is that of the colloidal metals. Those solids that are readily hydrated, like the metallic hydroxides and the insoluble acids, readily form jellies. Fruit juices will jelly only if there is sufficient of the fruit pulp in an unripe condition (pectin) to establish the filmlike walls of the jelly. On standing, a jelly often contracts, squeezing out some clear liquid on its surface. This process is called syneresis.

As a rule, gels result (1) from double decomposition; (2) from hydrolysis; (3) from the reduction of the salt of a metallo-acid.

References: Bancroft, *J. Phys. Chem.*, **18**, 549 (1914); Weiser, The Hydrous Oxides, Chap. I (1926); Bogue, Colloidal Behavior, Chap. XV (1924).

1. Production of Gels by Double Decomposition.

EXERCISE 102. GEL OF SILICIC ACID, $Si(OH)_4$

Prepare 50 cc. of a solution of sodium silicate by diluting commercial water glass to a density of 1.10. To this add about 50 drops of sulfuric acid, stirring constantly during the addition. Set the beaker aside for a day or two if necessary and then examine the clear gel of silicic acid. Tap the beaker with your knuckle and notice the ringing vibration of the gel. The gel forms best if the acid added is insufficient to decompose the silicate completely, the solution remaining slightly alkaline. The more dilute the solution the longer time is required for the jel to "set." The time also depends upon the nature of the acid added and the character of the electrolytes present.

References: Friend, V, 210; Mellor, VI, 290; Holmes, *J. Am. Chem. Soc.*, **40**, 1188 (1918); *J. Phys. Chem.*, **22**, 510 (1918).

EXERCISE 103. GEL OF CUPRIC HYDROXIDE, $Cu(OH)_2$

Prepare 50 cc. of a solution of copper acetate saturated at room temperature. Prepare also a solution of ammonia by diluting the concentrated reagent with an equal volume of water.

To 50 cc. of the solution of copper acetate add four drops of concentrated sulfuric acid and then, with constant stirring, slowly add 3 to 4 cc. of the dilute ammonia. The mixture sets to a light blue gel of copper hydroxide, that will stand up for a week or more under favorable conditions.

References: Mellor, III, 142; Friend, II, 278; Finch, *J. Phys. Chem.*, **18**, 26 (1914); Weiser, The Hydrous Oxides, p. 144 (1926); Paal and Steyer, *Kolloid-Zeit.*, **30**, 1 (1922).

Additional Exercise: Gel of mercuric oxide, Bunce, *J. Phys. Chem.*, **18**, 269 (1914).

2. Production of Gels by Hydrolysis.

EXERCISE 104. THE GEL OF STANNIC HYDROXIDE, $Sn(OH)_4$

Prepare a molar solution of crystallized stannic chloride and a four-molar solution of sodium acetate. Mix these two solutions in equal volumes. A firm white gel of stannic hydroxide forms almost immediately and is stable for a long time. The gel forms over a wide range in concentration, from about 35 per cent of the solution of stannic chloride up to about 60 per cent of the same solution.

References: Friend, V, 353; Mellor, VII, 408; Weiser, The Hydrous Oxides, p. 223 (1926); *J. Phys. Chem.*, **26**, 681 (1922); Ghosh and Dhar, *J. Phys. Chem.*, **31**, 649 (1927).

EXERCISE 105. THE GEL OF CHROMIC HYDROXIDE, $Cr(OH)_3$

The following method was apparently devised by Reinitzer and was subsequently studied by Bunce and Finch.

Twenty cubic centimeters of a 5 per cent solution of chromic chloride, to which 1 g. of sodium acetate had been added, is boiled in an Erlenmeyer flask provided with a funnel to serve as an air condenser. The boiling should be timed to 1 min. To one-half of the cooled solution, a solution of potassium hydroxide (1:3) is added until distinct alkalinity is reached. To the other half of the solution of chromic chloride ammonium hydroxide is added to alkalinity.

Both of these alkalies give solutions which spontaneously form opaque gels, in appearance differing from each other in color only. The gel from potassium hydroxide is green, while that from ammonium hydroxide is bluish violet.

References: Friend, VII (III), 36; Mellor, XI, 192; Reinitzer, *Chem. News*, **48**, 114 (1883); Bunce and Finch, *J. Phys. Chem.*, **17**, 769 (1913); Nagel, *ibid.*, **19**, 331 (1915); Weiser, The Hydrous Oxides, p. 100 (1926).

3. Production of Gels by Reduction of the Salts of Metallo-acids.

EXERCISE 106. THE GEL OF CHROMIC HYDROXIDE, $Cr(OH)_3$

A 6 per cent solution of potassium chromate is made just alkaline with sodium hydroxide. The containing beaker is then placed in a freezing mixture, and the chromate stirred until the solution has become cold. A slow current of hydrogen sulfide is then passed through the cold solution until it is saturated. The solution is then allowed to come to room temperature.

After standing at room temperature for 5 to 6 min., the greenish-yellow solution becomes green and gradually assumes an opalescent aspect, which disappears with the formation of a light-green opaque coloring. After standing quietly for several hours, a firm, dark green gel results in which little syneresis takes place.

References: Friend, VII (III), 39; Mellor, XI, 191; Cuy, *J. Phys. Chem.*, **25**, 415 (1921); Bjerrum, *Z. phys. Chem.*, **110**, 656 (1924).

EXERCISE 107. THE SOL AND GEL OF MANGANESE DIOXIDE, MnO_2

The Sol.—Five grams of commercial glucose dissolved in 25 g. of water is made alkaline with a 10 per cent solution of sodium hydroxide. The solution is stirred in a freezing mixture while 100 cc. of a 6 per cent solution of potassium permanganate is slowly added (during 10 min. and at a uniform rate).

The Gel.—As the mixture just described becomes warmer, it grows more and more viscous, until after 5 or 10 min. it jellies. After about ½ hr., syneresis starts and ultimately alters the gel structure. By the end of 3 hr., the solid phase has practically separated from the liquid phase, resulting in a small quantity of solid suspended in a clear liquid solution.

Alternate Method.—To 20 cc. of a 6 per cent solution of potassium permanganate (at room temperature) add three drops of glycerin. A sol results which will gelatinize in from 5 to 10 min. The gel resembles in every way the one obtained in the former experiment.

During the earlier stages of the liquefaction, observe the formation of globules of clear water (syneresis).

With a fine capillary pipette drop some of the liquid into a large beaker of water, observing the formation of vortex rings.

Add hydrogen peroxide to solutions of varying dilution, including very dilute ones (catalysis).

References: Mellor, XII, 261; Witzemann, *J. Am. Chem. Soc.*, **37,** 1079 (1915); **39,** 25 (1917).

EXERCISE 108. THE GEL OF FERROUS HYDROXIDE, $Fe(OH)_2$

Preliminary to the preparation of the gel of ferrous hydroxide, it will be necessary to prepare a solution of sodium ferrate, Na_2FeO_4. This can be done electrolytically according to the directions in Exercise 22.

Continue the electrolysis until a solution of sodium ferrate is obtained of a concentration approximately 8 per cent. This will be so deeply colored as to be quite opaque. The strength can be determined by titration with a standard reducing agent or by precipitating a measured volume of the solution with barium chloride and weighing the insoluble barium ferrate, $BaFeO_4$, after drying at 110° on a weighed filter paper.

Into a small beaker, measure 10 cc. of concentrated formic acid; and into another beaker, 20 cc. of the alkaline solution of sodium ferrate. Cool both solutions in a freezing mixture. While keeping the formic acid in the freezing mixture, add the solution of sodium ferrate to it drop by drop and with constant stirring. Keep the resulting solution cold overnight, by which time it should set to a very firm gel of nearly colorless ferrous hydroxide. During the addition of the ferrate, cease stirring for a moment and add a drop of the ferrate. A brown ring of ferric hydroxide may be observed which slowly widens until it disappears. Several drops added in rapid succession will give a series of concentric rings which disappear on stirring again.

References: No published data on the gel; the sol, Cotton and Mouton, *Ann. chim., phys.*, (8) **11**, 145 (1907).

IV. RHYTHMIC BANDS—LIESEGANG RINGS

The diffusion of a soluble salt through a gel is a slow process and under certain conditions is attended by some singular phenomena. Among the most interesting is the formation of the so-called Liesegang rings. If two salts that produce an insoluble precipitate on interaction are allowed to mix by diffusion through a gel, it would be expected that the precipitate would be uniformly distributed through the region of mixing. Under certain conditions, however, this is not the case, but the precipitation occurs in the form of distinct rings, each separated from the other by a zone of clear gel. The appearance of the product resembles in a striking way that of natural agate and onyx, and it is probable that the processes in the two cases are quite analogous. A number of theories have been proposed to account for the formation of the banded colloids, but no one of them seems to be entirely adequate as an explanation.

References: All texts on colloids; numerous articles by Liesegang and Hatschek in Kolloid-Zeitschrift; Holmes, *J. Am. Chem. Soc.*, **40**, 1187

(1918); Davies, *ibid.*, **44**, 2698, 2705 (1922); **45**, 2261 (1923); Daus and Tower, *J. Phys. Chem.*, **33**, 605 (1929).

EXERCISE 109. BANDED MERCURIC IODIDE, HgI_2

Prepare a convenient quantity (100 cc.) of a dilute solution of commercial water glass by diluting the commercial preparation to a density of 1.06 and an equal volume of normal acetic acid. Measure out 25 cc. of each of the solutions, stir them well together, and add enough potassium iodide to make the solution about 0.1 normal with respect to the latter salt. Obtain four good-sized test tubes and into each pour enough of the solution half to fill it. Into two of the tubes pour about 1 cc. of commercial glucose and shake thoroughly. Set the tubes aside until a stiff gel forms. Then add to each tube a layer of several centimeters deep of a 0.5-normal solution of mercuric chloride. In a few days, bands of bright red, crystalline mercuric iodide will form. They are usually more sharply defined in the tubes containing glucose.

References: Holmes, *J. Am. Chem. Soc.*, **40**, 1189 (1918); Hausmann, *Z. anorg. Chem.*, **40**, 110, 120 (1904).

EXERCISE 110. BANDED COPPER CHROMATE, $CuCrO_4$

In the manner described in the preceding exercise, prepare several tubes half filled with a gel obtained by mixing equal parts of water glass (density, 1.06) and acetic acid (0.5 normal) and with the addition of enough potassium chromate to make the solution 0.1 normal with respect to the latter salt. The chromate should be added to the water glass before the addition of the acetic acid.

After the mixture has set to form a gel, add to each of the tubes a solution of 0.5-normal copper sulfate.

The bands form in a few days and consist of amorphous copper chromate of a reddish-brown color.

References: Holmes, *J. Am. Chem. Soc.*, **40,** 1191 (1918).

V. CRYSTAL GROWTHS IN GELS

It has long been observed that very beautiful crystals sometimes develop in gels. Wonderfully fine crystals of sugar frequently grow in ordinary fruit jellies. Many splendid mineral crystals are embedded in silica and appear to have developed while the silica was in the state of a gel. For this geological aspect of the subject, consult the papers of Cornu in the first five volumes of *Kolloid-Zeitschrift.* The experiments on crystal growth require some time for the proper development of the crystals, but the technique of the method is very simple and easily acquired.

References: Holmes, *J. Franklin Inst.*, **184,** 743 (1917); Prat, *Kolloid-Zeit.*, **47,** 36 (1929).

EXERCISE 111. GOLD CRYSTALS

Prepare a solution of sodium silicate of density 1.06 by dilution of a good grade of the commercial article. Prepare also a supply of sulfuric acid approximately 3-normal. Pour 25 cc. of the dilute sodium silicate into an equal volume of the sulfuric acid and add 2 cc. of a 1 per cent solution of gold chloride, stirring well during the mixing. Divide the solution into two equal parts in test tubes that should not be more than about half filled and set the tubes aside in a cool place until a firm gel is formed. This may require upward of a week.

When a solid gel has been secured, nearly fill each test tube with a solution containing 8 per cent of oxalic acid, to act as a reducing agent. The growth of crystals can be observed within a few hours, and in a few days it will be complete. The crystals are observed best by viewing the test tube in bright sunlight.

References: Holmes, *J. Franklin Inst.*, **184**, 755 (1917); *Bull. soc. chim.*, **43**, 271 (1928).

EXERCISE 112. COPPER CRYSTALS

Prepare a supply of a dilute solution of sodium silicate (density, 1.06) by dilution of commercial water glass and pour it into an equal volume of 1-normal acetic acid. Add enough copper sulfate to make the solution 0.05-normal with respect to the copper sulfate. Fill several tubes half full of the solution and set them aside until a firm gel is obtained. To each test tube add a layer several centimeters deep of a 1 per cent solution of hydroxylamine hydrochloride. In several weeks, the tetrahedral crystals of copper may be observed, best in bright sunlight.

References: Holmes, *J. Franklin Inst.*, **184**, 756 (1917).
Additional Exercises: Crystals of silver and of lead.

EXERCISE 113. LEAD IODIDE CRYSTALS

In the manner described in the preceding exercises, prepare a gel of equal parts of sodium silicate (density, 1.06) and 1-normal acetic acid, adding 2 cc. of normal lead acetate for every 25 cc. of the mixture. Prepare the gel in half-filled test tubes and when it has set add to each tube a layer of a solution of 2-normal potassium iodide. A compact layer of lead iodide gradually forms just below the surface of the gel, followed by growths of fernlike and hexagonal crystals.

References: Holmes, *J. Franklin Inst.*, **184**, 758 (1917).
Additional Exercises: Crystals of silver sulfate, silver chromate, calcium tartrate, and copper tartrate.

VI. EMULSIONS

An emulsion consists of very small drops of one liquid (internal phase) dispersed throughout the body of a second liquid (external phase), the two liquids being insoluble or very sparingly soluble in each other. That the emulsion may be at all permanent, a third substance (emulsifying agent) must be added. The latter must be soluble in one of the liquids and not in the other. The one in which it is soluble tends to become the external phase. In ordinary emulsions, some form of soap or gelatin is the emulsifying agent, but a great variety of colloidal material may act the part.

The emulsion is made by violently shaking the constituents in a roomy flask, either by hand or, better, with a shaking machine or by beating them with some form of egg beater.

With a given emulsion, the most practical way to determine which is the external phase is to place a few drops of the emulsion on a clean glass plate and then carefully drop a single drop of one of the pure liquids (usually water) upon it. If the emulsion is merely diluted, the external phase and the added drop are the same. If the added drop merely remains an isolated drop upon the emulsion, the external phase and the drop are different liquids.

References: All general books on colloids; Bancroft, series of eight papers including comprehensive abstracts of significant work, *J. Phys. Chem.*, **16,** 177, 345, 475, 739 (1912); **17,** 501 (1913); **19,** 275, 513 (1915) **20,** 1 (1916). Newman, *ibid.*, **18,** 34 (1914); Briggs, *ibid.*, **19,** 210 (1915); Briggs and Schmidt, *ibid.*, **19,** 479 (1915); Ostwald, *Kolloid-Zeit.*, **47,** 131 (1929).

EXERCISE 114. EMULSIONS OF OIL IN WATER

Prepare a 5 per cent solution of sodium oleate (soluble in water but not in oil); or, if this is not available, a 5 per cent solution of hard soap. In a 250-cc. flask, put 2 cc. of the soap solution and add benzene in successive portions as follows: 5, 10, 20, 20, 20, 20, 30, and 50 cc. Shake the stoppered flask vigorously after each addition of benzene.

A stiff emulsion is obtained consisting of 99 cc. of benzene, emulsified in 1 cc. of water, by about 0.05 per cent (by weight) of sodium oleate. If less than about 80 per cent (by volume) of benzene is used, the emulsion will not be homogeneous but will consist of a lower watery layer on which floats a creamy emulsion.

With olive oil, a homogeneous emulsion can be obtained with 2 cc. of a 5 per cent solution of sodium oleate, and oil added to constitute from 76 to 96.8 per cent.

References: Newman, *J. Phys. Chem.*, **18,** 40 (1914); Langmuir, *Chem. Met. Eng.*, **15,** 468 (1916); Holmes and Cameron, *J. Am. Chem. Soc.*, **44,** 66, 71 (1922).

EXERCISE 115. EMULSIONS OF WATER IN OIL

If a solution of magnesium oleate is used instead of sodium oleate (soluble in oil but not in water), the oil becomes the external phase, and the water the internal.

Prepare a little magnesium oleate by treating a solution of sodium oleate with magnesium sulfate. Carefully wash the precipitate free from soluble impurities and dry at about 110°. Suspend 1 g. of the dry salt in 100 cc. of benzene and provide the flask with a reflux condenser. Boil until solution is obtained. Possibly the product is a colloidal dispersion rather than a very perfect solution. It has been found that a very little sodium oleate mixed with the magnesium oleate rendered the emulsions more permanent.

In a flask of about 150 cc. capacity, put 5 cc. of concentrated magnesium oleate solution, 5 cc. of benzene, 9 cc. of water, and 1 cc. of 1 per cent sodium oleate. Shake vigorously and at intervals of about 1 min. interrupt the shaking and add 2-cc. portions of water until a total of 20 cc. has been added. It is not practicable to go above 96 per cent of water, and emulsions containing about 75 per cent are more satisfactory.

Similar emulsions can be made by replacing the benzene with carbon disulfide, linseed oil, or turpentine.

Reference: Newman, *J. Phys. Chem.*, **18**, 49 (1914).

EXERCISE 116. EMULSIONS OF PAINT AND LINSEED OIL

Obtain a sample of mixed lead paint and also one of raw linseed oil. To 20 cc. of the mixed paint in a bottle, add 70 cc. of water in 5-cc. lots, shaking vigorously after each addition. This emulsion will contain about 72 per cent of water, and oil is the external phase, as will be shown by a drop test.

Shake together 20 cc. of raw linseed oil and 20 cc. of water, adding the water in small portions. A thick emulsion results without the addition of an emulsifying agent. In both cases, the emulsifying agent appears to be rosin that is present in the oil in solution but is insoluble in water. A little water is always present in mixed paint, and this is thoroughly emulsified during the grinding of the lead in oil.

Reference: Newman, *J. Phys. Chem.*, **18**, 51 (1914).

INDEX

A

Acid chlorides, 140
Acids, 82
  action of hydrogen peroxide on, 98
  chloro- and fluo-, 115
  metallo-, 92
  poly-, 119
  preparation of crystalline, 82
  thionic, 137
Air, carbon dioxide, 27
  moisture, 29
  oxidation, 20
  protection from action of, 20
Alloys, 74
  antimony-manganese, 77
  magnetic, 77
  sodium-lead, 76
  sodium-tin, 76
Aluminum, reductions by, 144
Alums, 105, 112
  preparation of, 110–111
Ammonates, 123, 126
Ammonia, action on salts, 122
  derivatives of, 126
    ammonobasic salts, 125, 132
  liquid, properties of, 122
    resemblance to water, 122, 123
    as a solvent, 76
    use in preparations, 130
Ammonium arsenitungstate, 121
Ammonium carbonate, preparation of solution of, 35
Ammonium chloride, recovery of, 36
Ammonium chlorostannate, preparation of, 119
Ammonium cupric chloride, 151
Ammonium cuprous trithiocarbonate, preparation of, 135
Ammonium hydroxide, double decomposition by, 123
Ammonium iron alum, 111
Ammonium phospho-vanadicotungstate, preparation of, 122
Ammonium phospho-vanadiotungstate, preparation of, 121
Ammonium phosphomolybdate, 119
  preparation of, 120
Ammonium sulfate, solubility of, 4
Ammonium tetrathio-cuprate, preparation of, 137
Ammonium tungstate, preparation of, 121
Ammonium vanadate, preparation of, 121
Ammonolysis, 125
Anions, salts of homoatomic, 75–76
Antimony-manganese alloys, 77
Antimony oxychloride, preparation of, 80
Antimony sulfate, preparation of, 32
Antimony sulfide, preparation of colloidal, 160
  use in preparations, 135, 136
Antimony trichloride, use in preparations, 81, 94

Arsenic, white, use in preparations, 44
Arsenic acid, preparation of crystalline, 83
Arsenious oxide, sublimation of, 49
  use in preparations, 44, 83
Astrakanite, 109

B

Barium dithionate, preparation of, 138
Barium ferrate, preparation of, 53, 95
Barium hydroxide, preparation of crystalline, 27
  use in preparations, 90, 134, 139
Barium hypophosphite, preparation of, 90
Barium sulfide, preparation of a solution of, 134
Barium thiosulfate, preparation of crystalline, 39
Barium trithiocarbonate, preparation of, 134
Base, action of a non-metal on a soluble, 89
  aquoammono, 132
  Millon's, 132
Beryllium acetate, basic, 81
Bomb, iron, 76
Borax, use in preparations, 99
Bredig, 162
Briggs, 165
Bromine, use in preparations, 71, 95
Bromostannic acid, preparation of, 119
Brownian movement, 156
Bunce, 168

C

Cadmium sulfide, preparation of colloidal, 162
Cadmium potassium cyanide, 112, 115
Calcium carbonate, preparation and solubility of, 35
Calcium chloride, preparation of a solution of, 37
Calcium cupric acetate, preparation of, 152
Calcium hydroxide, use in purification, 12
Calcium nitrate, preparation of, 19
Calcium sulfate, formation in preparation of cupric chloride, 37, 38
  solubility of, 34, 37
  solubility product of, 34
Camphor as a catalyst, 140
Carbon in iron, determination of, 151
Carbon dioxide, protection from, in air, 27
  solid, 45, 48
Carbon disulfide, use in preparations, 101, 134, 135
Carbon tetrachloride, action on oxides, 67
Carbonato-tetrammino-cobalti nitrate, preparation of, 128
Carbonyl chloride, action on oxides, 67
Carnallite, 103, 105, 108
Caro's acid, 96
Cassius, purple of, 158
Catalysts, poisoning of, 164
Celestite, 73
Cell, electrolytic, 97
Charcoal, catalysis by activated, 142
Chemical compounds (*see* Compounds)
Chlorides, of oxygen acids, 140
  preparation of, 62, 67
  volatile, 62, 69

Chlorine, preparation of, 63, 141
  use in preparations, 62, 140
Chloro-pentammino-chromic chloride, preparation of, 131
Chloro-pentammino-cobalti chloride, preparation of, 128
Chloroacids, 115, 118
Chloropurpureo-chromic chloride, 131
Chlorostannic acid, preparation of, 118
Chrome red, 79
  potassium alum, preparation of, 110
Chromic anhydride, use in preparations, 55, 99
Chromic chloride, preparation of anhydrous, 68
  use in preparations, 130
Chromic hydroxide, preparation of gel of, 168, 169
Chromic oxide, preparation of, 52
  use in preparations, 68, 146
Chromium, preparation of, 146
Chromyl chloride, preparation of, 143
Cobalt chloride, use in preparations, 128, 129
Cobalt nitrate, use in preparations, 113, 128
Cobaltiammine salts, 127
Collodion, preparation of a solution of, 165
Colloids, 155
  dialysis test for, 164
  precipitation by electrolytes, 161, 164
  preparation of, 157
  protecting, 159
Color of ferric salts, 31
Common ion effect, 106
Complex ion, 112, 124
Complex salt, 112
Compounds, binary, 57
  coordination, 81, 127
  dissociable, 100
  of halogens, 61
  intermetallic, 74
  metallo-organic, 152
  ternary, reduction of, 73
Conglomerate, 103
Coordination compounds, 81, 127
Copper, crystals of, 174
Copperas, 109
Cornu, 173
Crystal growth in gels, 173
Crystallization, 3
  after chemical removal of impurities, 12
  conditions for, 4
  of cupric sulfate, 11
  by diffusion, 39
  of potassium nitrate, 8
  of potassium sulfate, 6
  in presence of isomorphous impurities, 8
  from solutions of two salts, 103
  supersaturation in, 16
Crystals, hydrated, obtaining in good condition, 13
  mixed, 103
    (*See also* Drying of crystals)
Cupric ammonium chloride, 151
Cupric calcium acetate, preparation of, 152
Cupric chloride, preparation of, 36
Cupric chromate, preparation of banded, 172
Cupric hydroxide, preparation of gel of, 167
Cupric potassium chloride, preparation of, 151
Cupric sulfate, purification of, 9
  solubility of, 4
  tetramminate, 126
Cuprous ammonium trithiocarbonate, preparation of, 135

Cuprous chloride, oxidation of, 24
  preparation of, 24, 26
  use in preparations, 135
Cuprous iodomercurate, preparation of, 149
Cuprous mercuri-iodide, preparation of, 149
Cuprous potassium cyanide, 115

D

Decomposition, by ammonium hydroxide, 123
  double, 33, 64
  preparation, of gels by, 167
    of sols by, 160
Deliquescence, 18, 29, 31
Dialysis, purification of colloids by, 160, 161
  as test for colloids, 164
Dialyzer, preparation of, 164
Diffusion, crystallization by, 39
Dispersion of matter, 155
  by electricity, 162
Dissociable compounds, 100
Dissociation, pressure, 101
  thermal, 100
Distillation, 41
  of mercury, 41
  of nitrogen dioxide, 44
  of sulfur dioxide, 48
Double decomposition (*see* Decomposition, double)
Dry-ice, 45, 48
Drying, of crystals, antimony sulfate, 32
    barium hydroxide, 29
    hydrated ferric nitrate, 31
    hydrated sodium sulfate 14
    potassium sulfate, 7
  of efflorescent crystals, 14
  of gases, 45, 48

E

Efflorescence, 14
  of ammonates, 124
Electrical dispersion, 162
Electrochemical replacement, 147
Electrochemical series, 147
Electrodes, passive, 54
Electrolytic cell, 97
  preparations, 52
    apparatus for, 54
    (*See also* Barium ferrate; Lead chromate; Potassium persulfate)
Elements, union of, 58
Emulsions, 175
  of linseed oil, 177
  of oil in water, 175
  of paint, 177
  of water in oil, 176
Enantiotropy, 148
Eutectic, 75

F

Ferric acid, salts, 53, 95
Ferric ammonium alum, 111
Ferric hydroxide, preparation of colloidal, 161
  use in preparations, 95
Ferric nitrate, preparation of, 30
Ferric potassium alum, preparation of, 111
Ferric salts, color of, 31
Ferric sulfate, preparation of, 111
Ferrous chloride, oxidation of, 22
  preparation of, 22
Ferrous hydroxide gel, preparation of, 170
Ferrous potassium oxalate, 115
Ferrous sulfate, impurity in copper sulfate, 9–11
  oxidation of, 20
  preparation of, 20
  use in preparations, 109

Filters, preparation of, 6
Filtration, 5
Finch, 168
Fluoacids, 115–117
Fluorspar, use in preparations, 115
Fluosilicic acid, 115
Franklin, E. C., 125
Freezing mixture, 45, 48
Furnace methods, 50
Furnaces, bomb, 81
  care of, 51
  types of, 51

G

Gases, drying of, 45, 48
Gels, 156, 166
  crystal growths in, 173
Gibbs, W., 119
Gold, crystals of, 173
  mosaic, preparation of, 66
  preparation of colloidal, 158
Goldschmidt, 144
Grignard, 152
Gum mastic, 158

H

Halogen compounds, 61
Heat of formation of oxides, 144
Hexammino-chromic nitrate, 130, 131
Homoatomic anions, 75, 76
Hydrates, 13, 123
Hydrides, 69
Hydrobromic acid, preparation of, 70
Hydrofluoric acid, use in preparations, 116, 117
Hydrogen arsenate, preparation of, 83
Hydrogen bromide, preparation of, 70
Hydrogen fluoride, 116
Hydrogen iodate, preparation of, 84
Hydrogen iodide, preparation of, 72
  in preparation of phosphonium iodide, 102
Hydrogen peroxide, 96
  action on acids and salts, 98
  catalytic decomposition, 164
  use in preparations, 85, 99, 100
Hydrogen phosphate, preparation of crystalline, 83
Hydrogen sulfide, use in preparations, 65, 134, 137, 160, 162
Hydroiodic acid, preparation of, 72
  in preparation of phosphonium iodide, 102
Hydrolysis, 29, 125
  of ferric salts, 161
  of phosphorus tribromide, 71
  preparation, of gels by, 168
    of sols by, 161

I

Inoculation, 17
Intermetallic compounds, 74
Iodic acid, preparation of, 84
Iodine, as catalyst, 83
  use in preparations, 84, 85, 101
Ion, complex, 112, 124
  effect of common, 106
Iron, determination of carbon in, 151
  passive, 30, 54
  test for, 10, 11
Iron ammonium alum, preparation of, 111
Isomorphism, 8

K

Kainite, 109

L

Lead acetate, preparation of hydrated, 16
Lead chromate, preparation of 55, 79
  basic, preparation of, 79
Lead hydroxide, preparation of, 80
Lead iodide crystal growth in gels, 174
Lead nitrate, basic, preparation of, 79
Lead peroxide as oxidizing agent, 10
Lead-potassium alloys, 76
Lead-sodium alloys, 76
Lead tetraphenyl, preparation of, 152
Liesegang rings, 171
Lime, milk of, use in purification, 12
Linseed oil, emulsions of, 177
Liquids, volatile, distillation of, 46
  storage of, 46

M

Magnesium nitride, preparation of, 60
Magnesium oleate, preparation of and use of, 176
Magnetic alloys, 77
Manganese, preparation of, 145
Manganese-antimony alloys, 77
Manganese dioxide, preparation of gel and sol of, 169
  use in preparations, 64, 93, 138, 141, 145
Manganese dithioate, preparation of, 138
Manipulation, general methods of, 3
Mercuriammonium chloride, 132
Mercuric amino chloride, preparation of, 132
Mercuric chloride, use in preparations, 131, 132, 149
Mercuric chloride diammonate, preparation of, 131
Mercuric iodide, preparation of banded, 172
Mercuric sulfide, preparation of, 58
Mercuridiammonium chloride, 132
Mercury, distillation of, 41
  impurities in, 41
  use in preparations, 58, 116
Metallo-acids, 92
  production of gels by reduction of, 169
Metallo-organic compounds, 152
Metals, compounds between, 74
  preparation by reduction, 143–146
Metathesis (*see* Decomposition, double)
Millon's base, preparation of, 132
  salts of, 133
Mixed crystals, 103
Mohr's salt, 105
  preparation of, 109
Moisture, protection from atmospheric, 29
Molybdenum trioxide, use in preparations, 120
Monotropy, 149
Mosaic gold, preparation of, 66

N

Neutralization, 65, 77, 89
Nickel, test for, 134
Nitric acid, fuming, use in preparations, 84
Nitrogen dioxide, distillation and preparation, 44
Nonmetal, action on a soluble base, 89

O

Organo-metallic compounds, 152
Overvoltage, 65
Oxalic acid, use in preparations, 78
Oxidation, by air, prevention of, 20
  anodic, 55, 96–98
  electrolytic, 53–55, 96–98
Oxides, action of volatile chlorides on, 67
  heat of formation of, 144
  reduction by aluminum, 143–147

P

Paint, emulsions of, 177
Peptization, 157
Per-acids and salts, 96–100
Persulfuric acid, di-, 96
    preparation of potassium salt of, 97
  mono-, 96
Phosgene, action on oxides, 67
Phosphine, 90, 102
Phosphomolybdic acid, preparation of, 120
Phosphonium chloride, 101
Phosphonium iodide, preparation of, 101
Phosphoric acid, preparation of crystalline, 83
Phosphorus, white, use in preparations, 63, 83, 90, 101
Phosphorus pentasulfide, 133
Phosphorus tribromide, hydrolysis of, 71
Phosphorus trichloride, preparation of, 62
Platinum, preparation of colloidal, 162
Polyacids, 119
Potassium antimonite, preparation and oxidation of, 94
Potassium antimonyl tartrate, use in preparing colloids, 160
Potassium cadmium cyanide, 112, 115
Potassium chlorate, use in preparations, 87, 147
Potassium chloride, solubility of, 4
Potassium chlorostannate, preparation of, 119
Potassium chromate, reduction of, 169
  use in preparations, 55
Potassium chrome alum, preparation of, 110
Potassium cobaltinitrite, 112, 113, 115
Potassium cupric chloride, preparation of, 151
Potassium cuprous cyanide, 115
Potassium dichromate, reduction of, 110
  solubility of, 4
  use in preparations, 52, 79, 143
Potassium ferrate, preparation of, 95
Potassium ferricyanide, 112
  use in preparations, 114
Potassium ferrisulfide, preparation of, 136
Potassium ferrithiocyanate, test for ferric ion, 114
Potassium ferrocyanide, 112, 114
Potassium ferrous oxalate, 115
Potassium fluosilicate, preparation of, 117
Potassium fluotitanate, preparation of, 117
Potassium hydrogen pyroantimonate, preparation of, 94
Potassium iodate, preparation of, 147
Potassium iodide, use in preparations, 150

Potassium iodomercurate, preparation of, 150
Potassium-lead alloys, 76
Potassium mercuri-iodide, preparation of, 150
Potassium metavanadate, preparation of, 100
Potassium nitrate, crystallization of, 8
  solubility of, 4, 8
Potassium perchlorate, preparation of, 87
Potassium perchromate, preparation of, 99
Potassium permanganate, preparation of, 93
  reduction of, 169
  use in preparations, 64, 94
Potassium persulfate, preparation of, 97
Potassium pervanadate, preparation of, 100
Potassium phosphomolybdate, preparation of, 120
Potassium polyplumbide, 76
Potassium polystannide, 76
Potassium sulfate, crystallization of, 6
  solubility of, 4, 6
Potassium sulfide, preparation of a solution of, 134
Potassium tetroxalate, preparation of, 78
Potassium-tin alloys, 76
Potassium trithiocarbonate, preparation of, 134
Pressure, dissociation, 101
Purification, 3
  (*See also* Crystallization; Distillation; Filtration; Sublimation)
Purity of potassium sulfate, tests for, 7
Purple of Cassius, preparation of, 158
Pyrolusite (*see* Manganese dioxide)
Pyroxylen, use in preparing collodion solution, 165

R

Recrystallization (*see* Crystallization)
Reduction, aluminothermic, 143–147
  of metallo-acids, production of gels by, 169
  of oxygen salts, 88
  preparation of colloids by, 158
  of ternary compounds, 73
Reinitzer, 168
Replacement, electrochemical, 147
Rhythmic bands, 171
Rutile, use in preparations, 117

S

Salt, purification of common, 12
Salts, acid, 78
  action, of hydrogen peroxide on, 98
    of water and ammonia on, 122
  ammonia derivatives of, 126
  ammono basic, 125, 132
  basic, 79
  cobaltiammine, 127
  complex, 104, 112
  double, 103, 104, 112
    conditions for formation of, 105
  of ferric acid, 53, 95
  of homoatomic anions, 74–76
  hydrogen (acids), 82
  of metallo-acids, 92, 169
  of Millon's base, 133
  normal, 77
  oxidizing, 86

Salts, oxygen, 86
  of per-acids, 96
  of polyacids, 119
  preparation of, 77
  reducing, 87
  thio, 133
  of thionic acids, 137
  transition points in, 148
Schlippe's salt, preparation of, 135
Sealing tube, 46–47, 119
Seeding, 17
Silicic acid, 116
  crystal growth in gels of, 171–174
  preparation of gel of, 167
Silicon, preparation of, 146
Silver, preparation of colloidal, 159
Silver iodide, preparation of colloidal, 158
Silver iodomercurate, preparation of, 150
Silver mercuri-iodide preparation of, 151
Silver sodium thiosulfate, 115
Smith, E. F., 120
Sodium, test for, 94
Sodium arsenate, use in preparations, 121
Sodium chloride, solubility of, 4
  purification of, 12
Sodium cobaltinitrite, preparation of, 113
Sodium ferrate, preparation of, 54
  use in preparations, 170
Sodium-lead alloys, 76
Sodium nitrate, reduction of, 88
  solubility of, 4
Sodium nitrite, preparation of, 88
  use in preparations, 113, 129
Sodium nitroprusside, preparation of, 114
Sodium oleate, use in preparing emulsions, 175
Sodium perborate, preparation of, 99
Sodium polystannide, 76
Sodium polyplumbide, 76
Sodium silicate, use in preparations, 167, 172–174
Sodium silver thiosulfate, 115
Sodium sulfate, purification and drying of, 15
Sodium sulfite, use in preparations, 138
Sodium thioantimonate, preparation of, 135
Sodium thiosulfate, preparation of, 138
Sodium-tin alloys, 76
Sodium tungstate, preparation of, 121
Sol, 157
Solubility, of amorphous and crystalline forms of mercuric sulfide, 58
  as cause of deliquescence, 19
  of common salts, 4
Solubility curves, 4
  product, 33, 106
    applications, 34
    of calcium sulfate, 34
Stannic chloride, hydrolysis of, 168
  preparation of, 62
  use in preparations, 118
Stannic hydroxide, preparation of gel of, 168
Stannic sulfide, preparation of crystalline, 66
Stannous chloride, preparation of, 64
Stannous sulfide, preparation of, 64
Stibnite, 135
Strontium sulfate, reduction of, 73
Strontium sulfide, preparation of, 73

Sublimation, 49
  of arsenious oxide, 49
Sulfides, double, 136
Sulfo salts (*see* Thio salts)
Sulfur, preparation of colloidal, 158
Sulfur dioxide, action on manganese dioxide, 138
    on zinc, 91
  preparation, 48, 92, 138, 141
  reaction with chlorine, 140
  as reducing agent, 150
Sulfur monochloride, preparation of, 62
  reaction with oxides, 67
Sulfuryl chloride, preparation of, 140
Supersaturation, 16, 17
Suspensions, 155

T

Tartar emetic, use in preparing colloids, 160
Temperature of transition, 148
Tetrammino-cupri sulfate, 126
Tetraphenyl lead, preparation of, 152
Thermal dissociation, 100
Thermite welding, 144
Thio salts, 133
Thionic acids, salts of, 137
Tin-potassium alloys, 76
Tin-sodium alloys, 76
Transition temperature, 148
Trinitrito-triammino-cobalt, preparation of, 129
Tube, sealing, 46–47, 119
Tungsten trioxide, use in preparations, 121
Tyndall cone, 156

U

Union of two elements, 58

V

Vanadium pentoxide, use in preparations, 100, 121
Vanadium trioxide, preparation of, 122
Vermilion, preparation of, 58

W

Water, action on salts, 122
Water glass, use in preparations, 167, 172–174
Werner, A., 124

Z

Zinc, reaction with sulfur dioxide, 91
Zinc hyposulfite, preparation of, 91
Zsigmondy, 158

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